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# PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

# PCT

## INVITATION TO PAY ADDITIONAL FEES

(PCT Article 17(3)(a) and Rule 40.1)

To:  
ECOLAB INC.  
Attn. Sorensen, Andrew D.  
840 Sibley Memorial Highway  
Mendota Heights, MN 55118  
UNITED STATES OF AMERICA

Feb 10, 2003 - Inv. to Pay Fees.

Date of mailing (day/month/year)	27/12/2002
Applicant's or agent's file reference <b>1432W001</b>	<b>PAYMENT DUE</b> within <b>45</b> <del>XXXX</del> days from the above date of mailing
International application No. <b>PCT/US 02/ 21777</b>	International filing date (day/month/year) <b>10/07/2002</b>
Applicant  <b>ECOLAB INC.</b>	

**1. This International Searching Authority**

(i) considers that there are 2 (number of) inventions claimed in the international application covered by the claims indicated ~~XXXX~~ on the extra sheet:

and it considers that the international application does not comply with the requirements of unity of invention (Rules 13.1, 13.2 and 13.3) for the reasons indicated ~~XXXX~~ on the extra sheet:

(ii) ☒ has carried out a partial international search (see Annex) ☐ will establish the international search report on those parts of the international application which relate to the invention first mentioned in claims Nos.:  
**1-21, 30-38**

(iii) will establish the international search report on the other parts of the international application only if, and to the extent to which, additional fees are paid


**2. The applicant is hereby invited, within the time limit indicated above, to pay the amount indicated below:**

EUR 945,00 x 1 = EUR 945,00  
 Fee per additional invention      number of additional inventions      total amount of additional fees

Or, \_\_\_\_\_ x \_\_\_\_\_ = \_\_\_\_\_

The applicant is informed that, according to Rule 40.2(c), the payment of any additional fee may be made under protest, i.e., a reasoned statement to the effect that the international application complies with the requirement of unity of invention or that the amount of the required additional fee is excessive.

3. ☐ Claim(s) Nos. \_\_\_\_\_ have been found to be unsearchable under Article 17(2)(b) because of defects under Article 17(2)(a) and therefore have not been included with any invention.

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Authorized officer

**Emmanuel Cherquij** JAN - 2 2003

INTELLECTUAL PROPERTY





This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-21,30-38

Monoester peroxy dicarboxylic acid compositions suitable for use as disinfectants, containing diester dicarboxylate, hydrogen peroxide and water.

2. Claims: 22-29

Disinfectant solutions containing monoester percarboxylic acids in combination with anionic surfactants and/or amine oxide surfactants.

The common concept to all of claims 1-38 is therefore a composition containing a monoester percarboxylic acid, suitable for use as a disinfectant, as a solution to the need for high concentration monoester peroxy dicarboxylic acid compositions with good stability.

However, this common concept is not novel as it is disclosed in WO-A-98/28267 (see claim 30), which is also concerned with the need to provide higher concentration monoester peroxy dicarboxylic acid compositions (see abstract).

Since the general common concept is not novel, it can not be recognised and it appears that the requirement of unity of invention is not fulfilled ; Rule 13.1 PCT.

The application has been checked for identical or corresponding special technical features in the sense of Rule 13.2 PCT which could repair the finding of lack of unity, but no such features have been distinguished.

The Applicant is invited to pay an additional search fee for the invention of group 2.



**Annex to Form PCT/ISA/206  
COMMUNICATION RELATING TO THE RESULTS  
OF THE PARTIAL INTERNATIONAL SEARCH**

International Application No  
**PCT/US 02/21777**

1. The present communication is an Annex to the invitation to pay additional fees (Form PCT/ISA/206). It shows the results of the international search established on the parts of the international application which relate to the invention first mentioned in claims Nos.:  
**1-21, 30-38**
2. This communication is not the international search report which will be established according to Article 18 and Rule 43.
3. If the applicant does not pay any additional search fees, the information appearing in this communication will be considered as the result of the international search and will be included as such in the international search report.
4. If the applicant pays additional fees, the international search report will contain both the information appearing in this communication and the results of the international search on other parts of the international application for which such fees will have been paid.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 28267 A (SOLVAY INTEROX LTD) 2 July 1998 (1998-07-02) cited in the application abstract page 7, line 2 - line 36 page 9, line 36 -page 10, line 10 page 13, line 8 -page 14, line 14; claim 30; examples 8,22 ---	1-21, 30-38
A	WO 01 47359 A (HENKEL ECOLAB GMBH & CO. OHG) 5 July 2001 (2001-07-05)  claims 1,8,9,18-20,26; example 2 ---	1,4-13, 15, 30-32, 34-38
A	EP 0 967 203 A (SOLVAY) 29 December 1999 (1999-12-29)  column 4, line 50 -column 5, line 50 column 6, line 9 - line 43 ---	1-8, 12-15, 30-32, 34-38
A	WO 95 34537 A (SOLVAY INTEROX LTD) 21 December 1995 (1995-12-21)  page 5, line 29 -page 7, line 38 page 10, line 17 -page 11, line 18; claims 1,15; example 6 -----	1,2, 4-13,15, 30-38

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# Patent Family Annex

Information on patent family members

International Application No

PCT/US 02/21777

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9828267	A	02-07-1998	AU 734381 B2	14-06-2001
			AU 7872898 A	17-07-1998
			BR 9713781 A	24-10-2000
			EP 0946506 A1	06-10-1999
			WO 9828267 A1	02-07-1998
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WO 0147359	A	05-07-2001	DE 19962342 A1	12-07-2001
			WO 0147359 A2	05-07-2001
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			TR 200003829 T2	23-07-2001
			US 6423868 B1	23-07-2002
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			AU 2679495 A	05-01-1996
			DE 69508939 D1	12-05-1999
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			WO 9534537 A1	21-12-1995
			JP 10501805 T	17-02-1998
			US 6207108 B1	27-03-2001





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07C 409/24, 407/00, A01N 37/16</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/28267</b> <b>(43) International Publication Date:</b> 2 July 1998 (02.07.98)
<b>(21) International Application Number:</b> PCT/GB97/03461 <b>(22) International Filing Date:</b> 16 December 1997 (16.12.97)  <b>(30) Priority Data:</b> 9626637.4                      21 December 1996 (21.12.96)      GB  <b>(71) Applicant (for all designated States except US):</b> SOLVAY INTEROX LIMITED [GB/GB]; Baronet Works, Baronet Road, Warrington, Cheshire WA4 6HB (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CARR, Graham [GB/GB]; 5 Bishops's Court, Woolton, Liverpool L25 5HR (GB). JAMES, Alun, Pryce [GB/GB]; 28 Dowhills Road, Blun- dellsands, Liverpool L23 8SW (GB). MORTON, Kelly, Jane [GB/GB]; 12 Wilcote Close, Widnes, Cheshire WA8 9WP (GB). SANKEY, John, Phillip [GB/GB]; 46 Brook Drive, Great Sankey, Warrington, Cheshire WA5 1RY (GB). LAWTON, Valerie [GB/GB]; 72 Clarence Road, Grappen- hall, Cheshire WA4 2PQ (GB).  <b>(74) Agent:</b> PEARCE, Timothy; Solvay Interlox Limited, Patent Dept., P.O. Box 51, Moorfield Road, Widnes, Cheshire WA8 0FE (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PERCARBOXYLIC ACID SOLUTIONS		
<b>(57) Abstract</b> <p>Storage stable aqueous acidic solutions, often having a pH of up to 1 containing an ester peracid and/or an acid peracid can be obtained by reacting a diester satisfying the general formula <math>R^1-O-CO-R^2-CO-O-R^3</math> in which <math>R^1</math> and <math>R^3</math> each represents a alkyl group containing from 1 to 4 carbon atoms which may be the same or different and <math>R^2</math> represents an aliphatic alkylene group optionally unsaturated which may be linear or branched containing from 2 to 6 carbon atoms with aqueous hydrogen peroxide in the presence of an acid, such as sulphuric acid and permitting the compositions to progress towards equilibrium concentrations. By starting with a diester, perhydrolysis generates an ester peracid which is a particularly effective peracid. The process can be controlled to produce solutions containing a high peracid content and within a wide range of ratios of ester peracid to acid peracid.</p>		

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### Percarboxylic Acid Solutions

This invention relates to percarboxylic acid solutions and more particularly to their production from precursors comprising carboxylic acid esters.

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Percarboxylic acids, by virtue of their properties, are contemplated for application in a wide range of uses, for example as oxidants, as stain removers and as microbicides, amongst others. Many factors are taken into account in selecting which percarboxylic acid is employed for a particular application, including its effectiveness for the purpose, its ease of preparation, its stability, and its acceptability to the user. For example, a low molecular weight aliphatic monoperoxyacid such as peracetic acid has been the peracid of choice on a number of occasions, because it can be produced readily, is acknowledged to be effective and capable of being produced in stable solutions, and is acceptable to many users, but some producers of microbicidal compositions would prefer to employ a compound with less odour, in order to avoid possible offence or irritation to the final users of those compositions.

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A number of alternative percarboxylic acids have been disclosed hitherto in the literature that are derivable from dicarboxylic acids and derivatives thereof, including diperoxycarboxylic acids, their corresponding monoperoxy acids, and ester monoperoxycarboxylic acids.

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For example, European Patent application No. EP-A-0 166 571 to Unilever teaches the use of ester peracids of the general formula  $[RX]_m AOOH$ , where R is hydrocarbyl or alkoxyated hydrocarbyl, X is a heteroatom moiety, preferably oxygen, A is a wide range of organic moieties containing one or two carbonyl groups and m is one or two, for use in bleaching and laundry applications.

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European Patent Application No. EP-A-0 426 217 to Unilever teaches the use of ester peracids of the general formula  $X-O_2C-A-CO_3H$  where A is a C1 to C12 alkyl aryl or alkaryl radical and X is a C1 to C20 alkyl, aryl, alkyl aryl radical optionally including a heteroatom for use in bleaching and cleaning systems.

Both French Patent Application no. 2324626 and a paper by Nedelec et al, Synthesis, 1976, pp 821-3 teach a method for the preparation and isolation of ester peracids from the reaction between acid chlorides and hydrogen peroxide in organic solvents.

A paper by C. Lion et al, Bull. Soc. Chim. Belg. 1991, 100, pp.-559 discloses the preparation and isolation of ester peracids by the reaction between ester acid and hydrogen peroxide in the presence of high concentrations of sulphuric acid and quenching into ice. The ester peracids so produced are employed in the destruction of toxic organophosphorus compounds in aqueous alkaline solution.

Compositions containing ester percarboxylic acids and their preparation by reaction between a monoester of an aliphatic dicarboxylic acid and hydrogen peroxide have been described in a PCT Application, International Publication WO 95/34537 to Solvay Interlox Limited. Such compositions were shown to have no discernible odour and to be effective as a microbicide. Although the compositions exhibited a level of available oxygen (avox) stability that would enable to them to remain effective during several weeks storage, there is a continuing need to find ways of improving their storage capability, for example based on the total peracid content or total peroxygen content of the composition and/or extending the range of reagents from which they or related compositions can be produced.

It is an object of at least certain aspects of the present invention to provide a new or alternative process for the production of peracids of aliphatic dicarboxylic acids and their esters.

According to the present invention, there is provided a process for the production of aqueous percarboxylic acid solutions by reaction between a peroxygen compound and a precursor of the percarboxylic acid in the presence of an acid catalyst characterised in that the peroxygen compound is hydrogen peroxide and the precursor is an aliphatic diester satisfying the general formula  $R^1-O-CO-R^2-CO-O-R^3$  in which  $R^1$  and  $R^3$  each represents an alkyl group containing from 1 to 4 carbon atoms which may be the same or

different and  $R^2$  represents an aliphatic alkylene group which may be linear or branched containing from 2 to 6 carbon atoms and optionally unsaturated.

The selection of hydrogen peroxide to effect the peroxidation avoids the neutralisation or partial neutralisation that would arise if an alternative  
5 inorganic peroxygen compound like sodium percarbonate or sodium perborate were employed.

In a further aspect there is provided a composition comprising an ester, a peracid derivative of thereof, hydrogen peroxide and water characterised in that it comprises from 2 to 30% w/w hydrogen peroxide, 5 to 90% w/w water  
10 and 3 to 90% w/w of an aliphatic diester satisfying the general formula  $R^1-O-CO-R^2-CO-O-R^3$  in which  $R^1$  and  $R^3$  each represents an alkyl group containing from 1 to 4 carbon atoms which may be the same or different and  $R^2$  represents an alkylene group which may be linear or branched containing from 2 to 6 carbon atoms and optionally unsaturated, the % for the diester  
15 including the peracidic derivative thereof and any acidic derivative of the ester generated in situ.

Herein the compositions are often expressed in terms of the reactants that are introduced into the reaction mixture, namely the diester and hydrogen peroxide. It will be recognised that in the reaction mixture, a  
20 number of acid catalysed hydrolysis and perhydrolysis reactions take place, resulting in a complex mixture containing a residual concentration of the reactant diester, the corresponding monoester peroxy-carboxylic acid in which one or other of  $R^1$  and  $R^3$  groups have been substituted to convert the ester to a peroxyacid group and likewise the corresponding monoester carboxylic  
25 acid, and the corresponding diperoxy-carboxylic acid in which both  $R^1$  and  $R^3$  groups have been substituted to convert the ester to a peroxyacid group and likewise the corresponding dicarboxylic acid. As the reactions proceed, the mixture moves towards an equilibrium at which point the relative proportions of each constituent of the mixture depend on the relative proportions and  
30 concentrations of the diester and the hydrogen peroxide employed in the mixture before equilibration commences and the extent of decomposition of the peroxygen compounds subsequently. The rate at which the composition moves towards equilibrium depends on the prevailing temperature, the concentrations of the reactants and the concentration of the catalyst.

35 By controlling the composition of the reaction mixture expressed in terms of its reagents, and specifically by the choice of molar ratio of the diester to hydrogen peroxide and the extent of dilution of the mixture with

water, it is possible to control the ratio of monoester monopercarboxylic acid to other monopercarboxylic acid/dipercarboxylic acid constituents at equilibrium and during the move towards equilibrium. In particular the peroxygen species can be directed towards the acid/ monoperacid as the main or predominant peroxyacid species by diluting the mixture with at least a significant or preferably with a major fraction of water. The peroxyacid species can be directed towards the ester monoperacid species by employing high concentrations of the diester and hydrogen peroxide, preferably at or near an equimolar ratio and comparatively low concentration of water.

During the period in which the mixture is approaching equilibrium, the proportion of peroxygen species, as measured by the proportion of available oxygen (Avox), present as peroxyacid species increases. Since, for many purposes, peroxyacid species are more effective as eg a biocide or oxidant, it is desirable to store the mixture until a significant fraction of the developable peroxyacid species have been produced, such as at least 90% before use.

It will be recognised that there is a particular benefit in employing diester derivatives of dicarboxylic acids as substrate for the formation of peracid derivatives, namely that first perhydrolysis de-esterification reaction of such a substrate generates an ester peracid (a percompound containing an ester group and a peracid group) which has been found to be a particularly effective disinfectant compared for example with the corresponding acid peracid (a percompound containing a carboxylic acid group and a peracid group). Accordingly there is an immediate generation of the more effective peracid species from the diesters. By contrast, if a monoester derivative of a dicarboxylic acid is employed as substrate, the first perhydrolysis de-esterification reaction generates the acid peracid. It is highly desirable to produce compositions from diester substrates containing at least 0.1% and preferably at least 0.2% ester peracid. In a number of compositions according to the present invention, the ester peracid content is in the region of 0.3 to 3% w/w, and particularly in the region of 0.6 to 1.5% w/w, even after storage for several weeks such as 3 to 6. It is beneficial to select compositions containing at least 0.1% or preferably a higher concentration of ester peracid.

In a yet further aspect of the invention, there are provided compositions containing hydrogen peroxide, a peracid and an ester and hydrolysis and/or perhydrolysis derivatives thereof characterised in that they comprise at least 2% w/w hydrogen peroxide, preferably 2 to 30% w/w, at

least 3% w/w diester including hydrolysis and perhydrolysis derivatives thereof, preferably 3 to 90% w/w, of which at least 0.1 and preferably at least 0.2% w/w is an ester peracid.

The compositions produced from a diester and hydrogen peroxide will contain a residual concentration of hydrogen peroxide which will approach an equilibrium. Since hydrogen peroxide itself also enjoys bleach, oxidation and disinfectant properties, though often inferior to generated peroxyacid species, it is desirable to preserve the hydrogen peroxide content of the composition as well as encourage formation of peracids. The ability of the composition to preserve the content of the peroxygen species during preparation and storage of the compositions can be observed by measuring the total available oxygen (avox) retained in the composition and comparing it with the amount introduced in the hydrogen peroxide. Advantageously, it has been found that the invention process employing a diester peracid generator is a particularly effective means of preserving the avox of the resultant compositions.

The invention often employs fully saturated diesters, though it can employ unsaturated starting materials, such as the diesters of fumaric or maleic acid.

The present invention is particularly applicable to the production of peroxyacid-containing mixtures from diesters of linear dicarboxylic acids and especially to those in which  $R^2$  in the above-mentioned formula contains from 2 to 4 carbon atoms and to mixtures of any two or all three of them. An especially convenient diester starting material contains a mixture of diesters of succinic acid (10 to 20% w/w), glutaric acid (45 to 75% w/w) and adipic acid (20 to 33% w/w). The alkyl groups  $R^1$  and  $R^3$  are often either methyl or ethyl. It is often convenient for them to be the same, both within the same molecule and also in mixtures of dicarboxylic acids esters, but they can be different if desired, and mixtures of different alkyl groups for  $R^1$  and  $R^3$  can be employed. It is particularly desirable to employ dimethyl esters. A particularly convenient starting material comprises a mixture of the dimethyl diesters of succinic, glutaric and adipic acids. Other convenient starting materials comprise, for example, the dimethyl esters of the individual components of that mixture, such as dimethylsuccinate.

The invention process can be carried out at ambient temperature or at an elevated temperature, which in practice often means employment of a temperature selected within the range of from 10 to 50°C. Use of a yet higher

temperature tends to accelerate noticeably loss of available oxygen from the compositions. In many instances, either the entire production and storage equilibration period or the storage equilibration period alone is conducted at a temperature of between 15 and 30°C. Depending on the reagent and catalyst concentrations, as well as employing an elevated temperature, equilibration can be achieved at its shortest within a few hours and under less favourable conditions, equilibration can take several weeks. It is at the discretion of the producer as to the extent to which he adjusts the conditions to accelerate progress towards equilibration compared with progress at ambient. He may, in one variation, employ an elevated temperature such as from 30 to 50°C for a short period of for example 1 to 10 hours and for the remainder employ the natural ambient temperature of the mixture.

The acid catalyst is an inorganic or organic acid having a  $pK_a$  of about 3 or lower, and preferably having a  $pK_a$  of below 1. It is particularly desirable to employ a non-halide mineral acid such as sulphuric or phosphoric or sulphamic acid or an organic sulphonc acid such as methyl or toluene sulphonc acid or a cation exchange resin doped with acid (eg a resin available under the Trade Mark AMBERLITE IRA-93). The catalyst is desirably present at a concentration of from 0.05 to 10% w/w in the composition and in many instances from 0.1 to 2.5% w/w. When it is desired to produce solutions containing a relatively high concentration of peracid species, thereby employing reaction mixtures containing a major weight proportion of diester, it can be prudent to select the concentration of strong acid in inverse relationship to the concentration of hydrogen peroxide employed. This relationship can be described by the formula  $H \times C = 60$  to 150 and preferably 80 to 120, in which H is the weight concentration of hydrogen peroxide solution introduced, usually selected in the range of 50 to 85%, and C is the weight concentration of catalyst in the composition, usually selected in the range of from 0.75% to 2.25%. It will also be recognised that the strong acid can perform additional functions, depending on its concentration, such as improved lime-scale removal when present at a relatively high concentration, such as from 5 to 10% w/w of the composition.

The absolute amounts of diester and hydrogen peroxide and their ratio to each other in the reaction mixture can be varied within a wide range. It is strongly recommended that in addition to any other criteria mentioned herein, the absolute concentrations of the organic and hydrogen peroxide constituents within the mixtures are preferably selected so to avoid potentially

hazardous combinations by adoption existing guidelines for organics/peroxide/water compositions. As a general guide, it is highly preferable not to exceed at any time a hydrogen peroxide concentration of 30% w/w and preferable not to exceed 20% w/w. It is often desirable to employ at least 1 mole of hydrogen peroxide per mole of diester. In many instances, the hydrogen peroxide concentration in the mixture is selected in the range of from at least 2%, w/w, often at least 4%, w/w and, particularly, up to 16% w/w. It can be introduced into the composition at either a concentration calculated to achieve the desired concentration after mixture with remaining constituents or at a higher concentration to enable the balance of water to be added to achieve the desired concentration. In general, the proportion of diester in the reaction mixture is selected within the range of from about 3% w/w and often at least 5% w/w to 90% w/w.

In a number of embodiments, the proportion of diester in the mixture is selected in the range of at least 50%, particularly from about 70 to 85% by weight and especially from about 75 to 85% by weight, together with aqueous hydrogen peroxide providing up to 20% w/w  $H_2O_2$ . Preferably the amount of hydrogen peroxide is at least equimolar to the diester. By the choice of at least 70% of diester in the initial composition, it is usually possible to retain throughout the reaction the mixture as a one-phase system. It is particularly desirable to select in combination from around 75 to 85% diester and from 1 to 1.25 moles of hydrogen peroxide per mole of diester. In such embodiments, the mixture can generate, at equilibrium, desirably high concentrations of peracids and such conditions favour the generation preferentially of monoester peracids. Such peracids have been found to be particularly acceptable for employment in cleanser / disinfectant compositions in view of their capability to act as bleach oxidant for stains, their microbicidal properties and the absence of off-putting odours. In a number of these embodiments, the peracid concentration is high enough to provide a peracid avox in solution at equilibrium of between 1.5 and 3.5% by weight, which corresponds to a peracid concentration of between about 15 and 35% depending on the peracid avox itself and the peracid species present. It will be recognised that the concentrated compositions can be diluted by the presence of a minor amount of additional components to assist in wetting or cleansing of surfaces or articles or liquids, such as up to about 20% by weight of surfactants.

In other embodiments of the present invention, the compositions are relatively dilute, often containing from 50 to 90% water, in a number of instances at least 60% by weight of water, and in many instances at least 70% by weight of water, such as from 70 to 85% by weight of water. In such dilute embodiments, the compositions, initially, that is to say before equilibration commences, often contain hydrogen peroxide selected in the range of from at least 2% w/w and particularly 4 to 25% by weight and diester selected in the range of from at least 3% w/w and particularly 5 to 45% by weight. The weight ratio of diester to hydrogen peroxide initially in such dilute embodiments is often chosen in the range of from 4:1 to 2:3. Accordingly, in a number of selected embodiments, the proportion of water initially is from 75 to 85%, and the proportion of hydrogen peroxide is initially from 4 to 12% and the proportion of diester initially from 5 to 15%. In such compositions there is a greater propensity for the peracid species generated to comprise a significant fraction of acid peracid species in addition to monoester peracid species. As with the more concentrated embodiments, one or more surfactants can be incorporated, such as in amount of up to 20% often up to 10% by weight of the composition.

In yet further embodiments of the present invention, the producer can produce compositions which, if permitted to attain equilibrium, would have an intermediate water content, such as between 20 and 50%, an intermediate peracid avox concentration in the region of between about 0.5 to 1.2%. In such compositions the initial weight proportion of diester is often from 10 to 60% and the weight proportion of hydrogen peroxide is often from 10 to 30%.

In a further variation carried out in a plurality of stages, more concentrated reagents are employed in a first stage, and when the composition peracid content has progressed to a chosen intermediate fraction of that attainable at equilibration, in a second stage, the composition is diluted by introduction of sufficient water, and optionally hydrogen peroxide and/or diester and and/or preformed esteracid to prepare a more dilute composition, such as those described previously herein which desirably contain at least 50% water and of which many contain at least 75% water. Examples of such dilute compositions which can be prepared by the two stage route contain the concentrations and ratios of peracids, residual ester and hydrogen peroxide that are obtainable using the preferred dilute concentrations of hydrogen peroxide and diester before equilibration described hereinbefore. In the first stage, the reaction mixture expressed in



terms of its reactants desirably comprises at least 50% w/w diester and at least 1 mole of hydrogen peroxide per mole of diester, preferably at least an equimolar amount. The mixture is preferably stored until at least 75 molar % and more preferably at least 90 molar % of the equilibrium proportion of peracid species is attained. Preferably in the second stage, the amounts of diluent water, added reagents and optionally selected reaction products are so chosen as to produce a composition that is substantially at equilibrium or contains esteracid at above its equilibrium amount if produced in a single stage.

Amongst the variations in methods for producing the aqueous percarboxylic acid solutions of the present invention, and especially for producing compositions which contain a substantial fraction of water, such as those containing at least 50% by weight water, one variation which offers processing advantages comprises a two stage method, in the first stage of which aqueous hydrogen peroxide and the diester are agitated together to form a single phase, normally containing any stabilisers and optional surfactant, and in the second stage, the phase is diluted with water and optional constituents such as lime-scale remover and once again agitated until a single phase is obtained. It is especially desirable to conduct this process variation at above ambient temperature, such as from about 30 to 45°C. In this process variation, it is particularly beneficial to employ aqueous hydrogen peroxide which has a concentration selected in the range of from about 27% to 55% by weight  $H_2O_2$  and especially 33 to 40% by weight  $H_2O_2$ . It is of benefit to introduce the aqueous hydrogen peroxide gradually into the ester, and especially at a rate controlled such that the composition remains as a single phase. Likewise, when the aqueous hydrogen peroxide has been introduced, the water can be introduced at a rate similarly controlled to maintain a single phase. It will be recognised that the water introduction can commence before the hydrogen peroxide introduction has terminated, but that in such circumstances, it is preferable to control the rates of introduction of both constituents together to maintain a single phase.

It is an observed feature of the present invention that ester peracid generation from glutaric acid esters is favoured in comparison with its generation corresponding succinic or adipic acid esters, particularly when the diester constitutes the major weight fraction of the reaction mixture.

It is preferable to choose surfactants for incorporation into peracid compositions according to the present invention, whether they be

concentrated or dilute, which are compatible with peracid compositions, such as those described in WO 96/19558 to Solvay Interlox Limited. Herein the surfactants can be incorporated into preformed peracid solutions or present during the formation of the peracid solutions from the reagents.

- 5 Advantageously, if suitably chosen amounts and combinations of such surfactants as described therein are employed, they can perform additional functions such as thickening and can aid disinfection. Suitable classes of surfactants as described therein include non-ionic surfactants and particularly alcohol ethoxylates, anionic surfactants such as alkylsulphates and alkyl-  
10 benzene sulphonates, amine oxides and quaternary ammonium surfactants.

- Although the compositions produced by the invention process demonstrate a stability worthy of mention, for example by comparison with previously described methods for their preparation from other peracid precursors, including expressly the preparation of peracid compositions from  
15 monoesteracid compounds, their stability can be enhanced by the incorporation of a number of classes of compound identified below. These classes include hydroxy substituted aromatic carboxylic acids and ester derivatives thereof, particularly phenol carboxylic acids such as p-hydroxybenzoic acid and ester derivatives such as methyl or ethyl esters.  
20 They also include organic polyphosphonic acid sequestrants such as ethyldiene diphosphonic acid, and aminopolymethylenephosphonic acids, and mixtures thereof. Such compounds are often incorporated in an amount selected in the range of from 0.025 to 1%, and in many instances from 0.075 to 0.3% by weight of the composition.

- 25 The surfactants which can be employed herein can be nonionic, anionic, cationic, or amphoteric. Generally, the surfactants contain at least one hydrophobic group, e.g. an aliphatic hydrocarbon group containing at least 8 carbon atoms, and often from 10 to 26 carbon atoms, the aliphatic group often being acyclic, but sometimes containing an alicyclic group, or the hydrophobic  
30 group can be an alkaryl group containing at least 6 and preferably up to 18 aliphatic carbon atoms. The surfactant contains in addition at least one water-solubilising group for example a sulphonate, sulphate, or carboxylic group which is linked either directly or indirectly to the hydrophobic group. Linking members can include residues of polyhydric alcohols containing etheric or esteric  
35 linkages, for example derived from ethylene glycol, propylene glycol, glycerine or polyether residues. The surfactants can be soap or be synthetic, for example as described in chapter 2 of synthetic Detergents by A. Davidsohn and B. M.

Milwidsky, 6th Edition published in 1978 by George Godwin Limited, and methods of making them are described in chapter 5 of the same book. Amongst anionic surfactants described on pages 11-23 of the aforementioned book, sulphonates and sulphates are of special practical importance. The sulphonates include, for example, alkaryl sulphonates, and particularly alkyl benzene sulphonates, the alkyl group preferably being a straight chain containing 9 to 15 carbon atoms, of which one of the most commonly employed surfactants is linear dodecyl benzene sulphonate. Other anionic sulphonates which are useful in solutions herein include olefin sulphonates, obtained, for example, by sulphonating primary or secondary aliphatic mono-olefins, alkane sulphonates, especially linear alkane sulphonates, and hydroxy alkane sulphonates and disulphonates, especially 3-, 4-, and 5-hydroxy-n-alkyl sulphonates in which the alkyl group contains any even number from 10 to 24 carbon atoms. Other desirable anionic surfactants include alcohol sulphates, preferably linear, having a chain length of at least 10 carbon atoms and sulphated fatty acid alkanolamides. Other sulphates comprise sulphated nonionic surfactants as for example alkylphenoxyethylene oxide ether sulphate in which the alkyl groups contain from about 8 to 12 carbon atoms and there are 1 to 10 units of ethylene oxide in each molecule. Yet other sulphate surfactants comprise alkyl ether sulphates where the alkyl group contains from 10 to 20 carbon atoms, preferably linearly and each molecule contains from 1 to 10 preferably from 1 to 4 molecules or ethylene oxide. Further anionic surfactants include phosphate derivatives of the ethylene oxide based nonionic surfactants described herein.

It is of considerable advantage that at least a proportion of the anionic surfactant be in liquid form or readily liquifiable.

In many suitable classes of anionic surfactants the counter ion is a monovalent metal ion, often a sodium or potassium ion, or a quaternary ammonium cation derived for example from ethanolamine or isopropylamine.

In practice, cationic detergents are normally not present in the same composition as anionic surfactants, but when cationic detergents are used they are frequently quaternary ammonium salts such as tetraalkyl ammonium salts in which at least one of the alkyl group contains at least 10 carbon atoms or quaternary pyridinium salts substituted by an alkyl chain of at least 10 carbon atoms. Although quaternary ammonium halides, commonly chlorides, can be employed, particularly where the quaternary ammonium halide and ester peracid are combined shortly before use, in many embodiments it is preferred to employ non-halide quaternary ammonium salts. The use of non-halide quaternary ammonium salts is particularly

preferred where the solution containing the ester peracid and quaternary ammonium salt are to be stored for any significant period. The use of quaternary ammonium halides in such solutions for storage can cause decomposition of the ester peracid by oxidation of the halide. Examples of non-halide quaternary ammonium salts include sulphates, methosulphates, ethosulphates, hydroxides, acetates, saccharinates, phosphates and propionates.

A considerable proportion of nonionic surfactants suitable for use in the present invention comprises condensation products of ethylene oxide and possibly propylene oxide. One class of such nonionic surfactants which is of special importance comprises water soluble condensation products of alcohols containing from 8 to 18 carbon atoms with an ethylene oxide polymer often containing at least 5 moles of ethylene oxide per molecule of surfactants, e.g. from 7 to 20 moles of ethylene oxide. Other nonionic surfactants comprise water soluble condensates of alkyl phenols or alkyl naphthols with an ethylene oxide polymer normally containing from 5 to 25 moles of ethylene oxide per mole of alkyl phenol or alkyl naphthol. The alkyl group normally contains from 6 to 12 carbon atoms and is frequently linear. As an alternative to the hydrophobic moiety of the nonionic surfactant being linked to the hydrophilic moiety by an ether link as in alcohol or phenol/ethylene oxide condensates, the linkage can be an ester group. The hydrophobic moiety is normally the residue of a straight chain aliphatic acid containing from 8 to 22 carbon atoms and more particularly lauric, stearic and oleic residues. In one class of nonionic ester surfactants, the hydrophilic moiety often comprises polyethylene oxide, frequently in the ratio of from 5 to 30 moles of ethylene oxide per mole of the fatty acid residue. It will be recognised that both mono and di esters can be employed. Alternatively it is possible to employ as the hydrophilic moiety glycerol, thereby producing either mono or di glycerides. In a further group, the hydrophilic moiety comprises sorbitol. A further class of nonionic surfactants comprise alkanolamides which can be obtained when a C10 to C22 amide is condensed with a polyethylene oxide or polypropylene glycol hydrophilic moiety or moieties. Semi-polar detergents include water soluble amine oxides, water soluble phosphine oxides and water soluble sulphur oxides, each containing one alkyl moiety of from 10 to 22 carbon atoms and two short chain moieties selected from the groups of alkyl and hydroxyalkyl groups containing 1 to 3 carbon atoms.

Useful amphoteric surfactants include derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds in which the aliphatic moieties can be linear or branched, or two of which can join to form a cyclic

compound, provided that at least one of the constituents comprises or contains a hydrophobic group containing from about 8 to 22 carbon atoms and the compound also contains an anionic water solubilising group, often selected from carboxylic, sulphate and sulphonates.

- 5 Non-surfactant thickeners which may be employed comprise cross linked poly(acrylates), natural gums such as xanthan or rhamosan gum, cellulose derivatives such as carboxymethyl cellulose and silicates.

The method for disinfection according to the present invention comprises contacting the substrate to be disinfected with a solution of a storage stable,  
10 aqueous acidic solution of an ester peracid, or prepared from one. The solution may be employed without dilution, or may be diluted. When the compositions are diluted, the dilution is usually chosen to give a concentration of ester peracid in solution of between about 1 part per million and 10,000 parts per million, depending on the substrate.

- 15 The disinfecting method may utilise a very wide range of temperatures, typically ranging from about 4°C to the boiling point of the solution employed as a disinfectant. In many cases, especially if the disinfectant is being applied manually using, e.g. a cloth, the temperature will be limited by the maximum temperature which can be tolerated comfortably by the operative, and is unlikely  
20 to be greater than 60°C.

The disinfection process can be employed to treat a wide range of substrates. Many of the treatable substrates are either liquid or solid. A contaminated gaseous substrate can be treated conveniently by spraying with a dilute solution of the invention biocidal combination or by bubbling the gas  
25 through a bath of the invention peracid solution. One type of liquid substrate comprises micro-organism contaminated aqueous media such as recirculating process waters, or aqueous effluents prior to discharge. Such process waters and effluents occur in many different industries and can be contaminated by bacteria, algae, yeasts and more rarely by viruses. Without limiting to the  
30 following industries, contaminated process waters are prevalent during the processing of plant and animal materials, including the paper and pulp industries, food processing eg the sugar refining industry, brewing, wine-making and alcohol distilling industries, effluents from straw treatments, discharges from sewage treatment works, including partially treated or merely filtered discharges  
35 of sewage through pipelines extending out to sea, meat processing factories, carcass rendering activities and from the rearing of livestock. Other liquid substrates include irrigation water in the horticulture industry. A further

important source of contaminated aqueous media comprises cooling waters either industrially or arising from air conditioning units installed in large buildings, such as hotels, offices and hospitals. The invention compositions can be employed to treat non-aqueous liquid media, such as cutting oils.

5. Notwithstanding the foregoing, the invention compositions are seen as of particular value for disinfection in those areas which come into contact with humankind. Thus they can be employed to disinfect solids, including hard surfaces, or contaminated articles intended for re-use in the food processing, animal rearing, horticulture, catering, domestic or hospital environments. Hard  
10 surfaces can be made from metals, wood, ceramics, glass, and plastics and can include work-benches, walls, floors, sanitary ware (eg toilets and basins), plant or apparatus, containers, tools, machinery, plant and pipework. It will be recognised that for such hard surfaces, it is often convenient to immerse smaller articles in a solution of the invention biocidal composition, and for larger  
15 applications, a spray or the like distribution means can be easier to employ. The process can also be contemplated for disinfecting water absorbent materials such as infected linen or especially soiled babies' nappies that are often made from terry toweling. The invention compositions can be used to disinfect harvested plants or plant products including seeds, corms, tubers, fruit, and  
20 vegetables. Alternatively, the invention compositions can be used to treat growing plants, and especially crop growing plants, including cereals, leaf vegetables and salad crops, root vegetables, legumes, berried fruits, citrus fruits and hard fruits.

It will none the less also be recognised that the peracid solutions  
25 produced by the invention process may also be employed, if desired, for the other purposes for which peracids are used, including bleaching or as a bleach additive in washing processes.

Having described the invention in general terms, specific embodiments thereof are described in greater detail by way of example only.

30 Examples 1 to 6, and Comparisons CA1-6 and CB1-6  
In Example 1, a mixture of the dimethyl esters of respectively succinic, glutaric and adipic acids (16%, 58% and 26%, 106g), available under the name DBE from Dupont was stirred at ambient temperature (about 22°C) with demineralised water [DMW] (594.2g) and sulphuric acid (10g, 98% w/w) and  
35 aqueous hydrogen peroxide (285.6g, 35% w/w) was introduced slowly into the stirred mixture at such a rate that the solution temperature was kept at or close to 20°C. The resultant solution contained a significant concentration of

the corresponding monoperacid derivatives of succinic glutaric and adipic acids as the predominant peracid species and residual hydrogen peroxide. In Examples 2 to 6, the stabilisers shown in Table 1 below were mixed into portions of the solution obtained in Example 1.

5 The stability of the solutions was tested by transferring 120g of the solution into a screw capped HDPE bottle having a small vent hole and storing them in a dark temperature controlled enclosure. The available oxygen in the solution (avox) was measured initially and at 4 weekly intervals by a standard ceric sulphate titration method.

10 By way of comparison, the preparative process of Example 1 was followed but substituting for the DBE a mixture of monomethyl glutarate (53g), monomethyl adipate (26.5g) and monomethyl succinate (26.5g) from Aldrich Chemicals in CA and a mixture of succinic, glutaric and adipic acids (106g) obtained from BASF in CB. Similarly, solutions containing the same  
15 stabilisers were prepared from the unstabilised comparison solutions. The residual avox of the Comparison solutions is likewise shown in Table 1.

Table 1

No	Stabiliser		Storage	% Avox Retained		
	Type	weight g		Example	CA	CB
1	-	-	4	91.2	88.3	51.3
	-	-	8	89.9	76.7	28.3
2	pHBA	0.12	4	98.6	96.7	74.0
	"	0.12	8	97.5	95.9	50.2
3	HEDPA	0.20	4	96.7	90.9	57.7
	"	0.20	8	92.2	78.6	30.7
4	pHBA + HEDPA	0.12 + 0.20	4	99.6	98.5	77.3
	pHBA + HEDPA	0.12 + 0.20	8	100	96.3	54.6
5	ADPA	0.20	4	94.9	90.2	53.5
	"	0.20	8	89.3	78.7	30.6
6	ADPA + pHBA	0.20 + 0.12	4	100	97.4	77.6
	ADPA + pHBA	0.20 + 0.12	8	99.3	96.8	55.5

Herein, pHBA represents p-hydroxybenzoic acid.

HEDPA and ADPA each represents a commercially available grade of hydroxyethylidene-diphosphonic acid.

From Table 1, it can be seen that preparative method according to the present invention produced a more stable peracid solution with respect to the retention of avox than when the peracid solution was made from either the corresponding monoester of the dicarboxylic acid (CA) or the dicarboxylic acid itself (CB). It can also be seen that the same advantage was evident when the solution additionally contained stabilisers intended for peracids.

#### Examples 7 to 11

In these Examples, all of the constituents shown in Table 2 except the hydrogen peroxide were mixed together at ambient temperature in a high density polyethylene (HDPE) bottle and immediately after, the hydrogen peroxide was introduced very gradually to prevent the temperature rising more than a few degrees over 20°C. The surfactant was that available under the trade mark CAFLON NAS30. The bottle's cap was then fitted, and the solutions were analyzed for total avox (the avox from peracids and hydrogen peroxide), avox from solely peracids and by HPLC to distinguish between monoester peracid and acidperacids species present. The bottles were stored in the dark in a constant temperature enclosure set at 32°C. The residual total avox after 4 weeks' storage and the weight ratio (WR) of ester peracid : acid peracid are shown in Table 2.

Table 2

Constituent	Amount (g) present in				
	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11
DBE-5	120	75	75	22.5	22.5
H <sub>2</sub> O <sub>2</sub> 35%	21.43	64.3	21.43	64.3	21.43
DMW	8.57	10.7	53.57	63.2	106.07
H <sub>2</sub> SO <sub>4</sub> (98%)	1.5	1.5	1.5	1.5	1.5
pHBA	0.018	0.018	0.018	0.018	0.018
butyl triglycol	1.5	1.5	1.5	1.5	1.5
surfactant	3	3	4.5	1.5	1.5
% Avox Recovered	85.0	85.6	94.7	93.8	94.2
% peracid	4.5	9	3	2.6	1
WR ester peracid : acid peracid	3.0	1.6	0.7	0.2	0.2



From Table 2, it can be seen that peracid solutions can be obtained with an excellent retention of active oxygen species (as shown by the near 100% avox retention) over a wide range of ratios of diester substrate to hydrogen peroxide. From Table 2, it can also be seen that as the weight ratio of hydrogen peroxide to diester acid substrate increases and the dilution of the solution increases, there is a distinct tendency for acid peracid to be favoured relative to monoester peracid, whereas as the weight ratio of diester acid substrate to hydrogen peroxide increases and the concentration of substrate in the solution increases there is a distinct tendency for the monoester peracid to be favoured relative to the acid peracid.

In repeat trials at a higher addition of stabiliser, an enhanced avox stability was observed.

#### Examples 12 to 14

In Example 12, a relatively concentrated solution of peracids was obtained by introducing with agitation, concentrated hydrogen peroxide (4.7g, 85% w/w) into DBE (20g) and sulphuric acid (98% w/w, 0.2g) at ambient temperature, the rate of introduction being controlled to prevent the mixture temperature rising. The solution was stored in a screw capped HDPE bottle and the peracid and total avox concentrations were periodically measured by the standard methods used for Examples 7 to 11. The results for 1 day and 6 weeks are summarised below.

The process of Example 12 was repeated for Examples 13 and 14, but employing respectively 5.7g 70% w/w hydrogen peroxide and 0.3g sulphuric acid in Ex 13 and 7.99g hydrogen peroxide (50% w/w) and 0.4g sulphuric acid in Ex 14.

The results are summarised in Table 3 below.

Example No	Avox measured after					
	1 day		3 weeks		6 weeks	
	peracid	total	peracid	total	peracid	total
12	2.6	10.2	2.4	8.0	2.6	6.1
13	2.4	10.9	2.4	10.2	2.9	6.2
14	2.0	11.5	1.8	10.0	2.0	9.5

From Table 3, it can be seen that solutions generated in each Example contained within 1 day a high concentration of peracid species. The Table also shows that the compositions maintained their peracid concentration at a steady level for the 6 weeks storage. HPLC analysis of the solutions showed

that after 3 weeks, approximately 1/3rd of the diester had been converted to the ester peracid in each of Examples 12 to 14, 36%, 38% and 35% respectively and that after 6 weeks storage, the proportion of esterperacid had fallen by about 2%. The HPLC analyses also showed that at the concentrations of catalyst used, the solutions were substantially free from monomethylpersuccinic acid.

#### Examples 15 to 20

In these Examples, Example 12 was repeated but employing 0.4g of stated acid catalyst in the mixture and storage at either ambient or 40°C. The compositions were stored in dark at the formation temperature. The results are summarised in Table 4 below.

Table 4

Example no	Acid Catalyst	Temperature	Peracid Avox after	
			1 day	2 weeks
15	H <sub>2</sub> SO <sub>4</sub>	ambient	3.0	3.1
16	H <sub>2</sub> SO <sub>4</sub>	40	2.8	2.8
17	MSA	ambient	2.8	3.0
18	MSA	40	2.7	2.8
19	p-TSA	ambient	2.6	2.7
20	p-TSA	40	2.7	2.6

From Table 4, it can be seen that a very similar concentration of peracid is obtained using the range of catalysts and temperature conditions shown, and that the concentration is maintained, even at mildly elevated temperature over the period of time of the trial.

#### Examples 21 and 22

In Example 21, The process of Example 1 was repeated, but employing 100g of the mixed ester DBE.

In Example 22, a dilute peracid composition was produced in two stages. In the first stage, concentrated hydrogen peroxide solution (HTP grade, 85% w/w, 25g) was introduced slowly with stirring into DBE-5 (100g) containing conc. sulphuric acid (1g) and with cooling to prevent the mixture rising significantly above room ambient temperature, and this was stored overnight at ambient temperature, about 20-23C, by which time greater than 90% of the equilibrium amount of peracid had been produced. A fraction of the mixture (10g) was then diluted at ambient by introduction with stirring of demineralised water (71.4g) and a further amount of HTP (8g), to provide a

product which comprised in terms of the reactants 10% w/w diester and 10.5% hydrogen peroxide. The product was stored at ambient temperature in a screw capped HDPE bottle and analyzed for peracids periodically. The results are summarised in Table 5 below.

5 Table 5

	% w/w total peracids	% w/w ester peracid
Ex 21	1.0	0.2
Ex 22 after 1 week	3.0	2.7
Ex 22 after 3 weeks	1.0	1.0

It can be observed from Table 5 that the method employed in Example 22 resulted in the preparation of a composition containing a higher concentration of ester peracid, and that this advantage was maintained even after 3 weeks' storage by which time the total peracid content had fallen to that obtained by a one stage preparation route of Example 21.

#### Examples 23 to 28

In these Examples, compositions were made by stirring together in a flask at ambient temperature diester (DBE-5) or mixture of diesters (DBE) with laboratory grade sulphuric acid (98% w/w) demineralised water (DMW) and aqueous hydrogen peroxide (HTP - 85% w/w H<sub>2</sub>O<sub>2</sub>) until a single phase was observed, the stabilisers were introduced and the mixture stirred for a further 10 minutes. The constituents are summarised in Table 6 below.

Example No	23	24	25	26	27	28
Constituent	weight (g)					
DBE-5	14		30		160	
DBE		14		30		160
DMW	167.5	167.5	92	92	2.7	2.7
sulphuric acid	2	2	1.5	1.5	2	2
HTP	16.5	16.5	26.5	26.5	35.3	35.3
pHBA	0.2	0.2	0.15	0.15	0.2	0.2
ADPA	0.8	0.8	0.6	0.6	0.8	0.8

The compositions were then stored at ambient temperature in HDPE bottles.

#### 20 Examples 29 to 34 and Comparisons 35 to 37.

In these Examples and comparisons, the disinfectant capabilities of the compositions of Examples 23 to 28 were measured and compared with the performance of disinfectant compositions obtained in a similar manner, but

substituting glutaric acid for DBE-5 in respectively Example 23/25 (Comparison 35/36) and a mixture of succinic, glutaric and adipic acids for DBE in Example 24 for Comparison 37. The compositions were at least 1 month old when they were tested.

#### 5 Test Method

These tests were conducted according to the American Organisation of Analytical Chemists official method of analysis 960.09 of 1990, modified by i) employing sodium thiosulphate (50g/l) as neutraliser, together with catalase at 2-5 g/l a solution dilution of 9:1 and ii) culturing in a sterile Universal  
10 culture jar.

The results obtained with total peracid content of 100ppm are summarised in Table 7 below.

Example No	Composition obtained in	LRF against S.aureus	LRF against E.coli
29	23	1.85	2.39
30	24	3.61	2.15
31	25	2.05	3.49
32	26	3.81	3.31
33	27	2.32	2.89
34	28	4.16	4.23
Comp 35		1.16	3.53
Comp 36		0.93	3.25
Comp 37		1.03	3.46

From Table 6, it can be seen that the compositions according to the invention were effective disinfectants and that the benefit was especially  
15 observable in compositions which contained a significant fraction of ester peracid compared with compositions which contained a higher proportion of acid peracid. The compositions were also particularly effective against S.aureus and were generally of similar effectiveness against E.coli compared with the compositions generated from the dicarboxylic acid as starting  
20 material.

#### Examples 38 and 39

In these Examples, further compositions according to Example 23 were made by the same route, but substituting respectively 15g water by sulphamic acid and 18g water by phosphoric acid. The resultant compositions were able to  
25 function as both a disinfectant and lime-scale remover.

## Examples 40 and 41

In these Examples, a two stage route was employed to make disinfectant compositions. In the first stage, aqueous hydrogen peroxide (44.4g, 33.8%) was agitated with respectively DBE-5 or DBE (20g) at 35°C and a stabiliser system comprising 0.1% p-HBA and 0.2% ADPA until a clear single phase was observable and in the second stage at the same temperature was diluted with DMW (35g) at such a rate as to maintain a single phase system. It was observed that the first stage took about 1 hour in Example 40 and 75 minutes in Example 41, and the second stage took about 1 hour in each case.

This route represented a comparatively quick way to produce single phase compositions.

## Example 42

In this Example, the anti-microbial activity against mould spores *Aspergillus niger* of an invention composition was measured under a modified version of CEN method EN1040. The method was modified by testing 4 different concentrations of the peracid constituent instead of 3. The weighted mean counts were not calculated and the full Test report was not completed. The method was extended to include the evaluations of yeasts, because the specific method for yeasts had not been published by then.

The peracid composition which was tested was made using the method described in Example 1 using DBE-5 (424g), demineralised water (2377g), sulphuric acid (40g, 98%), H<sub>2</sub>O<sub>2</sub> (1142g, 35%) and p-HBA (4g). This was stirred for 4 hours at ambient to ensure complete homogeneity. The product contained 9% H<sub>2</sub>O<sub>2</sub> and 1.4% peracid at equilibrium.

The modified CEN method EN1040 was conducted under both clean and dirty conditions

The tests showed that the composition reduced the viable population of *Aspergillus niger* (spores) in the test by an LRF of above 4 under both clean and dirty conditions, not only when applied neat, but also when diluted by a factor of 4.

## Example 43

In this example, the general method of Example 1 was followed using diethyl glutarate (7g), H<sub>2</sub>O<sub>2</sub> (8.24g, 85%), sulphuric acid (1g, 98%) and demineralised water (83.8g). After stirring for 1 week at ambient, p-HBA (0.1g) and ADPA (0.17g) were added. The sample contained 7.82% H<sub>2</sub>O<sub>2</sub> and 0.88% peracid.

## Example 44

In this Example, the general method of Example 1 was followed at 30°C using dimethyl fumarate (7g), H<sub>2</sub>O<sub>2</sub> (85%, 8.24g), sulphuric acid (1g, 98%), demineralised water (83.8g) forming a suspension of diester in the aqueous medium. p-HBA (0.1g) and ADPA (0.17g) were added and after stirring for 7 hours at 30°C, the aqueous medium contained 0.3% peracid.

## Claims

1. A process for the production of aqueous percarboxylic acid solutions by reaction a peroxygen compound and a precursor of the percarboxylic acid in the presence of an acid catalyst characterised in that the peroxygen compound is hydrogen peroxide and the precursor is an aliphatic diester satisfying the general formula  $R^1-O-CO-R^2-CO-O-R^3$  in which  $R^1$  and  $R^3$  each represents an alkyl group containing from 1 to 4 carbon atoms which may be the same or different and  $R^2$  represents an alkylene group which may be linear or branched containing from 2 to 6 carbon atoms and optionally unsaturated.
2. A process according to claim 1 characterised in that the reaction mixture expressed in terms of its reactants comprises at least 3% diester, preferably selected in the range of from 5 to 90% w/w.
3. A process according to either claim 1 or 2 characterised in that the reaction mixture expressed in terms of its reactants comprises hydrogen peroxide selected in the range of up to 30% w/w and preferably not more than 20% w/w.
4. A process according to any preceding claim characterised in that the reaction mixture expressed in terms of its reactants comprises at least 4% w/w hydrogen peroxide.
5. A process according to any preceding claim characterised in that the reaction mixture expressed in terms of its reactants comprises at least 1 mole of hydrogen peroxide per 4 moles of diester.
6. A process according to claim 5 characterised in that the mole ratio of hydrogen peroxide : diester is selected in the range of from 10:1 to 1:4.
7. A process according to claim 6 characterised in that at least an equimolar amount of hydrogen peroxide is employed per mole of diester.

8. A process according to any preceding claim characterised in that the reaction mixture expressed in terms of its reagents comprises at least 50% w/w diester
- 5 9. A process according to claim 8 characterised in that the reaction mixture expressed in terms of its reagents comprises from 70 to 85% w/w diester, preferably 75 to 85% w/w diester and from 1 to 1.25 moles of hydrogen peroxide per mole of diester.
- 10 10. A process according to any of claims 1 to 7 characterised in that the reaction mixture expressed in terms of its reagents and water comprises from 50 to 90% w/w water, hydrogen peroxide selected in the range of from 4 to 25% w/w and diester selected in the range of from 5 to 45% w/w.
- 15 11. A process according to claim 10 characterised in that the weight ratio of diester to hydrogen peroxide is selected in the range of 4:1 to 2:3.
- 20 12. A process according to either of claims 10 or 11 characterised in that the reaction mixture expressed in terms of its reagents and water comprises 75 to 85% water and hydrogen peroxide selected in the range of from 4 to 12% w/w and diester selected in the range of from 5 to 15% w/w.
- 25 13. A process according to any of claims 1 to 7 or 10 to 12 characterised in that it is conducted in at least two stages, in the first stage of which a reaction mixture is employed which expressed in terms of its reactants comprises at least 50% w/w diester and at least 1 mole of hydrogen peroxide per mole of diester, preferably at least an
- 30 equimolar amount, which mixture is stored until at least 75 molar % of the equilibrium proportion of peracid species is attained and thereafter the mixture is diluted with water and optionally at least one of the reactants to produce a composition containing at least 50% and preferably at least 75% w/w water.
- 35



14. A process according to claim 13 characterised in that the diluted mixture contains, expressed in terms of the reactants, a total of 5 to 15% w/w diester and 4 to 12% w/w hydrogen peroxide.
15. A process according to any preceding claim characterised in that the solution is stored before use until its percarboxylic acid content reaches or exceeds at least 90% of the amount of percarboxylic acid present at equilibrium.
16. A process according to any preceding claim characterised in that aqueous hydrogen peroxide is introduced into diester at a rate controlled to maintain the mixture as a single phase.
17. A process according to claim 16 characterised in that the aqueous hydrogen peroxide has a concentration selected in the range of from 27 to 55% w/w  $H_2O_2$ .
18. A process according to claim 16 or 17 characterised in that water is introduced into a mixture of diester and hydrogen peroxide at a rate controlled to maintain the mixture as a single phase.
19. A process according to any of claims 16 to 18 characterised in that the proportion of water provided in total from the aqueous hydrogen peroxide and the water is at least 50% by weight of the final composition.
20. A process according to any preceding claim characterised in that the solution has a pH of from -2 to 1.
21. A process according to any preceding claim characterised in that in the formula,  $R^1$  and  $R^3$  are each selected from methyl and ethyl groups.
22. A process according to claim 23 characterised in that  $R^1$  and  $R^3$  are both methyl.
23. A process according to any preceding claim characterised in that in the formula  $R^2$  is saturated.

24. A process according to any preceding claim characterised in that in the formula  $R^2$  is selected from linear groups containing from 2 to 4 carbon atoms and mixtures of any two or all three of them.
25. A process according to any preceding claim characterised in that the reaction mixture contains up to 10% w/w of an acid introduced before, during or after the reaction.
26. A process according to any preceding claim characterised in that the reaction mixture contains from 0.1 to 2.5% w/w of an inorganic or organic acid catalyst having a  $pK_a$  of below 1.
27. A process according to any preceding claim characterised in that the reaction mixture contains from 0.025 to 1% w/w of at least one stabiliser selected from hydroxy-substituted aromatic carboxylic acids and their ester derivatives, and organic polyphosphonic acids or mixtures of any two or more thereof.
28. A process according to claim 27 characterised in that the hydroxy-substituted aromatic carboxylic acid comprises p-hydroxy benzoic acid, and the organic polyphosphonic acid comprises hydroxyethylidenediphosphonic acid or ethylene or cyclohexane diaminotetramethylene phosphonic acid or diethylene triaminopentamethylene phosphonic acid.
29. A process according to any preceding claim characterised in that the reaction mixture contains at least one surfactant introduced before, during or after the reaction.
30. A composition comprising an ester, a peracid derivative of thereof, hydrogen peroxide and water characterised in that it comprises at from 2 to 30% w/w hydrogen peroxide, 5 to 90% w/w water and 3 to 90% w/w of an aliphatic diester satisfying the general formula  $R^1-O-CO-R^2-CO-O-R^3$  in which  $R^1$  and  $R^3$  each represents an alkyl group containing from 1 to 4 carbon atoms which may be the same or different and  $R^2$  represents an alkylene group which may be linear or branched

containing from 2 to 6 carbon atoms and optionally unsaturated, the % for the diester including the peracidic derivative thereof and any acidic derivative of the ester generated in situ.

31. A composition according to claim 30 characterised in that it contains at least 0.1% w/w ester peracid and preferably from 0.3 to 3% w/w ester peracid
32. A composition containing hydrogen peroxide, a peracid and an ester and hydrolysis and/or perhydrolysis derivatives thereof characterised in that it comprises at least 2% w/w hydrogen peroxide, and at least 3% w/w diester including hydrolysis and perhydrolysis derivatives thereof, of which at least 0.1 is an ester peracid.
33. A composition according to any of claims 30 to 32 characterised in that the concentration of hydrogen peroxide is not more than 20% w/w.
34. A composition according to claim 33 characterised in that the concentration of hydrogen peroxide is from 4 to 12%.
35. A composition according to any of claims 30 to 34 characterised in that the concentration of diester and its derivatives is from 3 to 15% w/w.
36. A composition according to any of claims 30 to 35 characterised in that the weight ratio of diester and derivatives to hydrogen peroxide is selected in the range of from 4:1 to 2:3 and preferably from 3:2 to 2:3.
37. A composition according to claim 36 characterised in that the diester is a dimethyl.
38. A composition according to any of claims 30 to 37 characterised in that  $R_2$  in the formula for the diester represents an alkylene group containing from 2 to 4 carbons or a mixture of any 2 or 3 such diesters.
39. A composition according to any of claims 30 to 38 characterised in that it comprises additionally a surfactant, preferably up to 20% w/w.

40. A composition according to any of claims 30 to 39 characterised in that it contains from 0.025 to 1% w/w of at least one stabiliser selected from hydroxy-substituted aromatic carboxylic acids and their ester derivatives, and organic polyphosphonic acids or mixtures of any two or more thereof.
41. A composition according to any of claims 30 to 40 characterised in that it comprises additionally a non-halide mineral acid selected from sulphuric or phosphoric or sulphamic acid or an organic sulphonic acid at a concentration of from 0.05 to 10% w/w.
42. A composition comprising an ester, a peracid derivative of thereof, hydrogen peroxide and water characterised in that it comprises from 2 to 30% w/w hydrogen peroxide, 5 to 90% w/w water and 3 to 90% w/w of an aliphatic diester satisfying the general formula  $R^1-O-CO-R^2-CO-O-R^3$  in which  $R^1$  and  $R^3$  each represents an alkyl group containing from 1 to 4 carbon atoms which may be the same or different and  $R^2$  represents an alkylene group which may be linear or branched containing from 2 to 6 carbon atoms and optionally unsaturated, the % for the diester including the peracidic derivative thereof and any acidic derivative of the ester generated in situ and containing a C1 to C4 alcohol in the range of from 1 to 20% w/w and at a mole ratio to the aliphatic diester of greater than 1:1.
43. Use of a composition according to any of claims 30 to 42 as a disinfectant.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/03461

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C409/24 C07C407/00 A01N37/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 34537 A (SOLVAY INTEROX LTD) 21 December 1995 cited in the application see the whole document ---	1-44
A	FR 2 324 626 A (ANVAR) 15 April 1977 cited in the application see page 3; claims ---	1
A	LION C ET AL: "New decontaminants. Reaction of peroxyacid esters with toxic insecticides" BULL. SOC. CHIM. BELG. (BSCBAG,00379646);91; VOL.100 (7); PP.555-9, UNIV. PARIS 7;INST. TOPOL. DYN. SYST.; PARIS; 75005; FR. (FR), XP002059524 cited in the application see the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9534537 A	21-12-95	AU 2679495 A EP 0765309 A	05-01-96 02-04-97
FR 2324626 A	15-04-77	NONE	

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*Zur Erklärung der Zweibuchstaben-Codes, und der anderen  
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(54) Title: PEROXY ACIDS WITH EXCELLENT ADHESION TO SURFACES

(54) Bezeichnung: PERSÄUREN MIT GUTER HAFTUNG AUF OBERFLÄCHEN

(57) Abstract: The invention relates to the use of ester peroxy acids for improving surface perfusion during the disinfection of surfaces and to synergistic antimicrobial combinations of ester peroxy acids and additional constituents.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft die Verwendung von Esterpersäuren zur Verbesserung der Oberflächenbenetzung bei der Desinfektion von Oberflächen sowie synergistische antimikrobielle Kombinationen von Esterpersäuren mit weiteren Komponenten.

### **„Persäuren mit guter Haftung auf Oberflächen“**

Die vorliegende Erfindung betrifft die Verwendung von Esterpersäuren zur Verbesserung der Oberflächenbenetzung bei der Desinfektion von Oberflächen sowie synergistische antimikrobielle Kombinationen von Esterpersäuren mit weiteren Komponenten.

Im Stand der Technik ist bekannt, daß man für die Oberflächendesinfektion Persäureverbindungen, wie z.B. Peressigsäure, einsetzen kann. Persäureverbindungen sind sehr wirksame Biozide. Dennoch wird der Geruch der meisten Persäuren als störend empfunden, insbesondere wenn es um die Anwendung in Systemen geht, in denen Menschen der Geruchsbelastung ausgesetzt sind.

Deshalb war es erstrebenswert, alternative Desinfektionswirkstoffe zu finden. Da Desinfektionswirkstoffe mit oxidativem Wirkmechanismus meist innerhalb kurzer Zeit Keime abtöten können, würde man diese gerne für die Oberflächendesinfektion einsetzen. Die im Stand der Technik bekannten Alternativen zu Persäuredesinfektionswirkstoffen mit oxydativem Wirkungsmechanismus, wie Hypochlorit, Ozon, Chlordioxid, haben ebenfalls Nachteile in der Anwendung, wie beispielsweise geruchliche Belastung, Bildung von ökotoxischen Verbindungen, die das Abwasser belasten können, Bildung von Gasen, die humantoxisch wirken können, sowie schwierige Handhabung, Erzeugung und Stabilität.

Die Patentschrift EP 765 309 betrifft lagerstabile, wäßrige Esterpersäurelösungen sowie deren Verwendung als Desinfektionsmittel. Diese Esterpersäurelösungen haben gemäß der zitierten Patentschrift reduzierten Geruch gegenüber den üblicherweise verwendeten aliphatischen C<sub>1</sub>- bis C<sub>3</sub>- Persäuren.



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Dadurch wird erreicht, daß derartige Esterpersäurelösungen in Bereichen eingesetzt werden können, in denen bisher vom Einsatz von Persäuren aufgrund des störenden Geruches Abstand genommen wurde.

Die zitierte Schrift lehrt uns somit, daß das Geruchsproblem, das die üblichen Persäuren mit sich bringen, durch Einsatz von Esterpersäuren gelöst werden kann.

Es ist jedoch nirgends in der Schrift erwähnt, daß bei Einsatz von üblichen Persäuren ein weiterer gravierender Nachteil besteht. Die üblicherweise zur Desinfektion verwendeten Persäuren haben nur eine geringe Affinität zu Oberflächen, was dazu führt, daß bei ihrer Verwendung in Desinfektionsvorgängen die Desinfektionslösungen nur kurze Zeit an den zu behandelnden Oberflächen haften und danach auf den Boden tropfen oder von der zu behandelnden Oberfläche ablaufen. Aufgrund dieses schnellen Abtropfens oder Ablaufens ergibt sich eine nur kurze Kontaktzeit der Persäurelösung mit den zu behandelnden Oberflächen, was sich nachteilig auf das Desinfektionsergebnis auswirkt. Um ein optimales Desinfektionsergebnis zu erreichen, ist es erstrebenswert, die Kontaktzeit des Desinfektionswirkstoffes mit der zu behandelnden Oberfläche zu verlängern. Um diese Aufgabe zu lösen, werden in der Praxis, beispielsweise bei der aseptischen Abfüllung, oberflächenbenetzende Hilfsmittel zugesetzt. Die bevorzugten oberflächenbenetzenden Hilfsmittel führen mit Persäureverbindungen oft zu wenig stabilen Formulierungen. Außerdem sind zusätzliche Hilfsmittel unter ökonomischen, ökologischen und toxikologischen Gesichtspunkten in vielen Fällen nur als zusätzlicher Ballast zu sehen. Deshalb bestand ein Bedarf nach oxidativ wirkenden Wirkstoffen, die, für sich alleine betrachtet, Oberflächen besser benetzen.

Dementsprechend war es Aufgabe der vorliegenden Erfindung nach Persäureverbindungen zu suchen, die bei ihrer Verwendung das Haftvermögen an und/oder die Benetzung von Oberflächen besonders vorteilhaft beeinflussen.

Gegenstand der vorliegenden Erfindung ist die Verwendung von Formulierungen, die mindestens eine Esterpersäure der allgemeinen Formel



enthalten, worin R eine Alkylgruppe von 1 bis 4 Kohlenstoffatomen, wobei es bevorzugt ist, daß R eine Methylgruppe ist, und x eine Zahl von 1 bis 4 ist, wobei es besonders bevorzugt ist, daß die Formulierungen eine oder mehrere Esterpersäuren ausgewählt aus Persuccinsäuremonomethylester, Perglutarsäuremonomethylester, Peradipinsäuremethylester, Perbernsteinsäuremonomethylester enthalten, und vorzugsweise in der Formulierung 0,001 bis 15 Gew.-%, besonders bevorzugt 0,1 bis 5 Gew.-% einer oder mehrerer Esterpersäuren, bezogen auf die gesamte Formulierung, vorliegen, zur Verbesserung der Oberflächenbenetzung bei Verwendung derartiger Formulierungen im Vergleich zur Verwendung gleicher molarer Mengen der entsprechenden Persäuren alleine oder in Kombination mit moläquivalenten Mengen des korrespondierenden Alkohols bei der Oberflächen-desinfektion und/oder -reinigung. Es ist bevorzugt, daß bei der erfindungsgemäßen Verwendung auf nicht waagerecht angeordneten Oberflächen eine längere Kontaktzeit der erfindungsgemäß zu verwendenden Formulierungen zur Oberfläche besteht, als bei Verwendung gleicher molarer Mengen der entsprechenden Persäuren allein oder in Kombination mit moläquivalenten Mengen des korrespondierenden Alkohols. Es ist ebenfalls bevorzugt, daß bei der erfindungsgemäßen Verwendung ein besserer antimikrobieller und/oder zusätzlicher Reinigungseffekt erzielt wird im Vergleich zur Verwendung gleicher molarer Mengen der entsprechenden Persäuren alleine oder in Kombination mit moläquivalenten Mengen des korrespondierenden Alkohols. In einer weiteren bevorzugten Ausführung der erfindungsgemäßen Verwendung ist es möglich, bei niedrigerer Konzentration und/oder reduzierter geruchlicher Belastung zumindest die gleiche antimikrobielle Wirksamkeit zu erreichen, wie bei Verwendung gleicher molarer Mengen der entsprechenden Persäuren alleine oder in Kombination mit moläquivalenten Mengen des korrespondierenden Alkohols.

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Es ist weiterhin bevorzugt, daß in den erfindungsgemäß zu verwendenden Formulierungen zusätzlich 1 bis 50 Gew.-% Wasserstoffperoxid, bezogen auf die gesamte Formulierung, enthalten sind.

Außerdem ist es bevorzugt, daß in den erfindungsgemäß zu verwendenden Formulierungen zusätzlich 0,1 bis 25 Gew.-% wenigstens einer nicht veresterten Persäure, bezogen auf die gesamte Formulierung, enthalten sind, wobei es besonders bevorzugt ist, daß als nicht veresterte Persäure eine Persäure ausgewählt aus den Monoperoxycarbonsäuren und/oder Diperoxydicarbonsäuren enthalten ist, wobei es ganz besonders bevorzugt ist, daß die in den erfindungsgemäß zu verwendenden Formulierungen vorliegenden nicht veresterten Persäuren ausgewählt sind aus Peressigsäure, Perpropionsäure, Persuccinsäure, Perglutarsäure, Peradipinsäure, Perbernsteinsäure,  $\omega$ -Phthalimidoperoxihexansäure, Perfettsäure mit 8 bis 18 Kohlenstoffatomen pro Molekül oder Mischungen der genannten Persäuren.

In einer weiteren bevorzugten Ausführung der vorliegenden Erfindung sind, bezogen auf die gesamte erfindungsgemäß zu verwendende Formulierung, zusätzlich 5 bis 50 Gew.-% wenigstens einer organischen Säure, die keine Persäure darstellt und vorzugsweise ausgewählt ist aus Essigsäure, Propionsäure, Succinsäure, Glutarsäure, Adipinsäure, Bernsteinsäure,  $\omega$ -Phthalimidohexansäure, Fettsäuren mit 8 bis 18 Kohlenstoffatomen pro Molekül oder aus Mischungen dieser Säuren enthalten.

Es ist weiterhin bevorzugt, daß die erfindungsgemäß zu verwendende Formulierung zusätzlich wenigstens ein Hydrotrop enthält, wobei es besonders bevorzugt ist, daß das eingesetzte Hydrotrop ausgewählt ist aus der Gruppe der anionischen Tenside, ganz besonders bevorzugt aus den Sulfonaten/Sulfonsäuren und insbesondere aus Cumol-, Xylol-, Octyl-, Naphthyl- und Alkylbenzolsulfonaten/Sulfonsäuren, wobei im letzten Fall die Alkylgruppe zwischen 6 und 16 Kohlenstoffatomen beinhaltet, oder Mischungen dieser Verbindungen und/oder weite-

ren Verbindungen die als Lösevermittler für längerkettige Persäuren geeignet sein können.

Es ist weiterhin bevorzugt, daß die erfindungsgemäß zu verwendenden Formulierungen zusätzlich wenigstens eine Komponente mit komplexierenden Eigenschaften für mehrwertige Metallionen enthalten. Besonders bevorzugt ist in den erfindungsgemäß zu verwendenden Formulierungen als Komponente mit komplexbildenden Eigenschaften eine Verbindung enthalten, die ausgewählt ist aus Nitrilotriessigsäure, Ethylendiamintetraessigsäure, Methylglycindiessigsäure, Gluconsäure, Zitronensäure, Dicarboxymethyl-L-glutaminsäure, Serindiessigsäure, Imidosuccinsäure, und der Gruppe der Polycarbonsäuren und Phosphonsäuren sowie jeweils deren Salzen.

Als Polycarbonsäuren kommen beispielsweise Polyacrylsäuren und Copolymere aus Maleinsäureanhydrid und Acrylsäure sowie die Natriumsalze dieser Polymeren in Betracht. Handelsübliche Produkte sind z. B. Sokalan® CP 5 und PA 30 von BASF, Alcosperse® 175 und 177 von Alco, LMW® 45 N und SPO2 ND von Norsohaas. Zu den geeigneten nativen Polymeren gehören beispielsweise oxidierte Stärke (z. B. DE 42 28 786) und Polyaminosäuren wie Polyglutaminsäure oder Polyasparaginsäure, z. B. der Firmen Cygnus, Bayer, Rohm & Haas, Rhône-Poulenc oder SRCHEM.

Als Phosphonsäuren kommen beispielsweise 1-Hydroxyethan-1,1-diphosphonsäure, Diethylentriaminpentamethylenphosphonsäure oder Ethylendiamintetramethylenphosphonsäure sowie jeweils deren Alkalisalze in Frage.

In einer besonders bevorzugten Ausführung der vorliegenden Erfindung bilden die in den erfindungsgemäß zu verwendenden Formulierungen vorliegenden Esterpersäuren zusammen mit

- a) wenigstens einer Fettsäure, in der vorzugsweise 8 bis 12 Kohlenstoffatome enthalten sind, wobei die Fettsäure besonders bevorzugt Octansäure ist, und/oder

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b) wenigstens einem Hydrotrop, das besonders bevorzugt Cumol-, Octyl-, Xylol-, Naphthyl- oder Alkylbenzolsulfonat mit 4 bis 16 Kohlenstoffatomen in der Alkylgruppe ist, und/oder

c) wenigstens einer tensidischen Schaumträgerkomponente, wobei vorzugsweise die tensidische Schaumträgerkomponente ein gegenüber Oxidationsmitteln stabiles Aminoxidderivat ist und es besonders bevorzugt ist, daß das Aminoxidderivat ein Trialkylaminoxid mit einer 8 bis 20 Kohlenstoffatome enthaltenden Alkylgruppe und zwei Alkylgruppen mit einer geringeren Anzahl an Kohlenstoffatomen in der Alkylkette darstellt, wobei die beiden kürzeren Alkylgruppen gleich oder verschieden sein können, wobei es ganz besonders bevorzugt ist, daß das Aminoxidderivat Talgfett-bis-(2-hydroxyethyl)-aminoxid, Oleyl-bis-(2-hydroxyethyl)-aminoxid, Kokos-bis-(2-hydroxyethyl)-aminoxid, Tetradecyldimethylaminoxid und/oder Alkyldimethylaminoxid, das 12 bis 18 Kohlenstoffatome in der Alkylkette aufweist, ist,

eine antimikrobielle synergistisch wirkende Zusammensetzung und/oder eine schaumbildende Kombination zur Reinigung und/oder zur Desinfektion von Oberflächen.

Zusätzliche bevorzugte tensidische Zusätze zu erfindungsgemäß zu verwendenden Formulierungen sind ausgewählt aus den Gruppen der anionischen, kationischen, nichtionischen, amphoteren Tenside, Eiweißhydrolysate, der Alkylaminoxide, der Silikonverbindungen und der Phosphorsäureester und deren Salzen.

Als anionisches Tensid können beliebige, auf dem Gebiet der Wasch- und Reinigungsmittel übliche anionische Tenside eingesetzt werden, die auch, wie oben erwähnt eine Wirkung als Hydrotrop entfalten können, wie z. B. C<sub>8</sub>-C<sub>18</sub>-Alkylsulfate, C<sub>8</sub>-C<sub>18</sub>-Alkylethersulfate, C<sub>8</sub>-C<sub>18</sub>-Alkansulfonate, C<sub>8</sub>-C<sub>18</sub>- $\alpha$ -Olefinsulfonate, sulfonierte C<sub>8</sub>-C<sub>18</sub>-Fettsäuren, C<sub>8</sub>-C<sub>18</sub>-Alkylbenzolsulfonate, Sulfonbernsteinsäuremono- und -di-C<sub>1</sub>-C<sub>12</sub>-Alkylester, C<sub>8</sub>-C<sub>18</sub>-Alkylpolyglykoethercarboxylate, C<sub>8</sub>-C<sub>18</sub>-N-Acyltauride, C<sub>8</sub>-C<sub>18</sub>-N-Sarkosinate, C<sub>8</sub>-C<sub>18</sub>-Alkylisethionate sowie Gemische der voranstehenden.

Vorzugsweise werden als nichtionische Tenside in den erfindungsgemäß zu verwendenden Formulierungen Alkylpolyglukoside, die üblicherweise durch Kondensation von Fettalkoholen mit Glukose oder Polyglukose großtechnisch zugänglich

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und in verschiedenen Varianten im Handel erhältlich sind, eingesetzt. Beispiele von Alkylpolyglukosiden, die sich für den erfindungsgemäßen Einsatz besonders gut eignen, sind die Produkte Glukopon® 600 der Firma Henkel und Triton® BG10 der Firma Röhm & Haas.

Weitere bevorzugte nichtionische Tenside sind alkoxylierte Alkylalkohole mit 8 bis 22 Kohlenstoffatomen in der Alkylkette befindet, wobei insbesondere wenigstens eine Verbindung aus den Gruppen der gemischten Ethoxylate/Propoxylate von verzweigten oder unverzweigten Alkylalkoholen mit 8 bis 22 Kohlenstoffatomen in der Alkylkette und der endgruppenverschlossenen Ethoxylate von verzweigten oder unverzweigten Alkylalkoholen mit 8 bis 22 Kohlenstoffatomen in der Alkylkette enthalten ist, und ganz besonders bevorzugt wenigstens eine Verbindung aus den Gruppen ethoxylierter und propoxylierter Alkylalkohole mit 12 bis 22 Kohlenstoffatomen im Alkylteil, der Butylether ethoxylierter Alkylalkohole mit 12 bis 22 Kohlenstoffatomen im Alkylteil und Methylether ethoxylierter Alkylalkohole mit 12 bis 22 Kohlenstoffatomen im Alkylteil enthalten ist, wobei im speziellen Fall Butylether und Methylether des ethoxylierten 2-Octyl-1-dodecanols enthalten sind. Nichtionische Tenside, die zur Herstellung der erfindungsgemäßen Formulierungen besonders gut geeignet sind, sind beispielsweise Plurafac® LF 403, Plurafac® 431 der Firma BASF sowie Dehypon® LT 104 und Dehypon® G 2084 der Firma Henkel.

Vorzugsweise werden als Phosphorsäureester in den erfindungsgemäß zu verwendenden Formulierungen Phosphorsäureesterverbindungen eingesetzt, worunter sich vorzugsweise zumindest ein Salz eines Phosphorsäurepartialesters befindet, wobei besonders bevorzugt wenigstens ein Alkalisalz eines Phosphorsäurepartialesters von alkoxyliertem Alkylphenol vorliegt.

Bei den Phosphorsäureestern handelt es sich um tensidische Substanzen, die sich vorzugsweise von langkettigen aliphatischen oder araliphatischen Alkoholen ableiten. Als besonders geeignet haben sich die Salze der Phosphorsäurepartialester und hier insbesondere die von alkoxylierten Alkylphenolen erwiesen. Vorzugsweise werden als Alkalisalze die Natrium- und Kaliumsalze verwendet, von denen wiederum die Kaliumsalze besonders bevorzugt werden. Tensidisch wirk-

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same Phosphorsäurepartialester, wie sie bevorzugt erfindungsgemäß verwendet werden, sind im Handel erhältlich. Ein Beispiel eines erfindungsgemäß besonders gut brauchbaren Wirkstoffs dieser Art ist das Produkt Triton® H 66 (Röhm & Haas).

Es ist bevorzugt, daß die erfindungsgemäß zu verwendenden Formulierungen als wäßrige Lösung, Gel, Emulsion, Paste, Dispersion, Pulver, Granulat, Schuppen, Perlen, Tabletten, blockartige Formkörper oder als Extrudat vorliegen.

Es ist weiterhin bevorzugt, daß die erfindungsgemäß zu verwendenden Formulierungen im Bedarfsfall vor dem Einsatz für Reinigungs- und/oder Desinfektionszwecke mit Wasser verdünnt werden, wobei es besonders bevorzugt ist, daß der Verdünnungsfaktor zwischen 10 und 10.000 liegt.

Vorzugsweise werden die erfindungsgemäß zu verwendenden Formulierungen in konzentrierter oder mit Wasser verdünnter Form auf die zu behandelnden Oberflächen durch Tauchen und/oder über Hilfsmitteln, die ausgewählt sein können aus Pinsel, Schwamm, Rollen, Tücher, Lappen, Bürsten, Wischer, Gummi, Mops, Flachwischbezüge, Sprühvorrichtung aufgetragen, wobei es besonders bevorzugt ist, daß auf der zu behandelnden Oberfläche wäßrige, gel-, schaum-, suspensions-, emulsions- oder pastenförmige Filmbildung erfolgt und die erfindungsgemäß zu verwendenden Formulierungen im Bedarfsfall rheopexe oder thixotrope Eigenschaften aufweisen.

Es ist weiterhin bevorzugt, daß die erfindungsgemäß zu verwendenden Formulierungen als kombinierte Reinigungs- und Desinfektionsmittel eingesetzt werden, wobei es besonders bevorzugt ist, wenn die erfindungsgemäß zu verwendenden Formulierungen zur Reinigung und/oder Desinfektion von Oberflächen, die Materialien ausgewählt aus Kunststoff-, Textilfasern, Glas, Keramik, Porzellan, Quarz, Granit, Metall, Holz als Hauptbestandteile enthalten, verwendet werden.

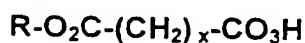
Es ist bevorzugt, daß mit den erfindungsgemäß zu verwendenden Formulierungen Tierhufe, Haut, Geschirr, Textilien, Fliesen, Wände, Bodenbeläge, Holz- und

Steinflächen und -böden und -wände, Arbeitsflächen, Maschinenaußenflächen, Kleinteile von Maschinen, medizinische Instrumente und/oder Geräte, beschichtete und/oder unbeschichtete Tanks und/oder sonstige Behälter, Leitungen, Transportbänder, Gebinde, Lebensmittel, wie Obst und Gemüse, gereinigt und/oder desinfiziert werden. Dabei ist es besonders bevorzugt, wenn die erfindungsgemäß zu verwendenden Formulierungen zur Desinfektion von Mehrweg- und Einweggebinden aus Glas, Karton und/oder Kunststoff verwendet werden.

Eine bevorzugte Spezialanwendung der erfindungsgemäß zu verwendenden Formulierungen findet im Verfahrensablauf der aseptischen oder keimarmen Abfüllung von mikrobiologisch sensiblen Lebensmitteln, insbesondere von Eistee, Apfelschorle, alkoholhaltigem und/oder alkoholfreiem Bier, Milch, Joghurt, statt, wobei es hier besonders bevorzugt ist, daß die Lebensmittelverpackungen vor der Abfüllung der mikrobiologisch sensiblen Produkte mit erfindungsgemäß zu verwendenden Formulierungen behandelt werden und/oder die im Bereich der keimarmen Abfüllung befindlichen Oberflächen, inclusive der lebensmittelführenden Leitungen, Tanks, Geräte, Maschinen, Transportbänder und -anlagen, Rinser, Herstellvorrichtungen für Gebinde mit erfindungsgemäß zu verwendenden Formulierungen behandelt werden.

Dementsprechend werden die erfindungsgemäß zu verwendenden Formulierungen vorzugsweise in Haushaltsbereichen, in der lebensmittelherstellenden und -verarbeitenden Industrie, wie z.B. in der Getränke-, Milch-, Fischindustrie und in Schlachtereien sowie in Großküchen, in der Gebäudereinigung, beispielsweise durch professionelle Dienstleister, im Krankenhaus, in Großwäschereien und in der Landwirtschaft verwendet.

Ein weiterer Gegenstand der vorliegenden Erfindung sind antimikrobielle synergistisch wirkende Zusammensetzungen zur Reinigung und Desinfektion von Oberflächen, die mindestens eine Esterpersäure der allgemeinen Formel





worin R eine Alkylgruppe von 1 bis 4 Kohlenstoffatomen und x eine Zahl von 1 bis 4 ist, kombiniert mit einer Komponente, die ausgewählt ist aus

- a) wenigstens einer Fettsäure mit 8 bis 18 Kohlenstoffatomen, vorzugsweise 8 bis 12 Kohlenstoffatomen, wobei besonders bevorzugt ist, daß die Fettsäure Octansäure ist, und/oder
- b) wenigstens einem Hydrotrop, das vorzugsweise ausgewählt ist aus Cumolsulfonat, Octylsulfonat, Naphthylsulfonat, Xylolsulfonat oder Mischungen dieser Verbindungen, sowie anderen Lösevermittlern, die als Lösevermittler für länger-kettige Persäuren geeignet sind, und/oder
- c) wenigstens einer tensidischen Schaumträgerkomponente, die vorzugsweise ein gegenüber Oxydationsmitteln stabiles Aminoxidderivat ist, wobei es besonders bevorzugt ist, daß das Aminoxidderivat ein Trialkylaminoxid mit einer 8 bis 20 Kohlenstoff-Atome enthaltenden Alkylgruppe und zwei Alkylgruppen mit einer geringeren Anzahl an Kohlenstoffatomen in der Alkylkette, wobei die beiden kürzeren Alkylgruppen gleich oder verschieden sein können und besonders bevorzugt ist, wenn das Aminoxidderivat Talgfett-bis-(2-hydroxyethyl)-aminoxid, Oleyl-bis-(2-hydroxyethyl)-aminoxid, Kokos-bis-(2-hydroxyethyl)-aminoxid, Tetradecyldimethyl-aminoxid und/oder Alkyldimethyl-aminoxid, die 12 bis 18 Kohlenstoffatome in der Alkylkette aufweisen, ist.

Die antimikrobielle synergistisch wirkende Zusammensetzung enthält vorzugsweise, bezogen auf die gesamte Formulierung, 0,0001 bis 15 Gew.-%, besonders bevorzugt 0,1 bis 5 Gew.-% eines oder mehrerer Esterpersäuren sowie 0,01 bis 15 Gew.-%, besonders bevorzugt 1 bis 10 Gew.-% wenigstens einer Fettsäure und/oder 0,01 bis 25 Gew.-%, besonders bevorzugt 1 bis 15 Gew.-% wenigstens eines Hydrotrops und/oder 0,01 bis 15 Gew.-%, besonders bevorzugt 1 bis 10 Gew.-% wenigstens einer tensidischen Schaumträgerkomponente, wobei die bevorzugten Ausführungen der Fettsäuren, Hydrotrope und der tensidischen Schaumträgerkomponenten bereits vorne im Text genannt sind. Die beanspruchten antimikrobiell synergistisch wirkenden Zusammensetzungen werden vorzugsweise in den vorne im Text beschriebenen Verwendungen eingesetzt.

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Es ist ganz besonders bevorzugt, wenn die erfindungsgemäßen synergistisch antimikrobiell wirkenden Zusammensetzungen zusätzliche wirksamkeitssteigernde, anionische Tenside wie Alkylbenzolsulfonsäure oder deren Salze oder weitere Alkylsulfonsäuren oder deren Salze enthalten.

In speziellen synergistisch wirkenden Zusammensetzungen erreicht man darüber hinausgehende Effekte, wenn man die erfindungsgemäßen Zusammensetzungen mit anderen Persäuren, wie beispielsweise  $\omega$ -Phthalimidoperoxihexansäure kombiniert.

## Beispiele

### Beispiel 1:

In einem Versuch wird das Ablaufverhalten unterschiedlicher Persäure-Lösungen untersucht.

Als Ausgangsbasis für die Versuche werden Formulierungen P1, P2, P3 und P4, die sich nur in Art und Menge der verwendeten Persäure unterscheiden, in 5%iger wäßriger Lösung sowie in Form des Konzentrats verwendet. Die Inhaltsstoffe dieser Formulierungen sind in Tabelle 1 enthalten.

Tabelle 1:

Persäure-Mittel P1, P2, P3, P4 für die Versuche zum Ablaufverhalten

Persäureanteil	P1	P2	P3	P4
Perglutarsäuremono-methylester (10 %ig)	100	-	-	-
Peressigsäure (10 %ig)	-	100	-	-
Perglutarsäure (10 %ig)	-	-	100	90
Methanol	-	-	-	10

Je 200 mL der Persäure-Formulierungen P1, P2, P3 und P4 werden als 5%ige wäßrige Lösungen sowie in Form des Konzentrats in 250 mL Bechergläsern angesetzt.

Im Anschluß werden vorher entfettete und gewogene Edelstahlbleche in diese Lösungen getaucht.

Im nächsten Schritt werden die Bleche aus den Lösungen mit einer Pinzette entfernt.

Man läßt die restliche Lösung 10 Sekunden lang ablaufen und wiegt danach die Bleche erneut. Die so ermittelte, auf den Blechen verbleibende Restmenge, ist ein Kriterium für die Affinität der Versuchslösung zur Oberfläche bzw. für die Anhaftung auf der Oberfläche.

Die auf diese Weise ermittelten Haftmengen sind in Tabelle 2 zusammengefaßt

**Tabelle 2:**

Auf den Blechen verbleibende restliche Haftmengen in Abhängigkeit von der Persäure-Rezeptur in konzentrierter Form oder in 5%iger wäßriger Lösung

	P1	P1 5%	P2	P2 5%	P3	P3 5%	P4	P4 5%
<b>Haftmengen in mg</b>	<b>365</b>	<b>141</b>	<b>231</b>	<b>121</b>	<b>264</b>	<b>125</b>	<b>260</b>	<b>126</b>

Es zeigt sich, daß die erfindungsgemäß zu verwendenden Formulierungen von Esterpersäuren eine bessere Benetzung bzw. Affinität zu Oberflächen haben, als die entsprechenden Vergleichsformulierungen.

**Beispiel 2:**

Die antimikrobielle Wirksamkeit von verschiedenen Kombinationen von Persäureestern mit ausgewählten Zusatzstoffen wurde im quantitativen Suspensionstest nach DVG untersucht.

Als Testkeime zur Ermittlung der bakteriziden Wirksamkeit wurden *Staphylococcus aureus* und *Escherichia coli* herangezogen. Als Testkeime zur Ermittlung der fungiziden Wirksamkeit wurden *Saccharomyces cerevisiae* sowie *Aspergillus niger* herangezogen. Die geprüften Rezepturen sind in Tabelle 1 enthalten. Die Ergebnisse im quantitativen Suspensionstest können aus Tabelle 2 sowie aus Tabelle 3 entnommen werden.

**Tabelle1:** Rezepturen für die mikrobiologische Untersuchung

Rohstoff	Rezeptur 1	Rezeptur 2	Rezeptur 3	Rezeptur 4	Vergleichs-Rezeptur
Perglutar säuremono-methylester (10 %ig)	80	80	80	80	100
Alkylbenzolsulfon-säure	10	-	-	10	-
Dimethylkokosamin-oxid	-	10	-	-	-
Natrium-Octyl-Sulfonat	-	-	16	6	-
Octansäure	-	-	4	4	-
Wasser	10	10	-	-	-

**Tabelle 2:** Ergebnisse der mikrobiologischen Untersuchungen gegen Bakterien

Produkt	[AWK] %	Staphylococcus aureus ATCC 6538 (K 3212) Inoculum $7,05 \times 10^8$ KBE / ml		Escherichia coli ATCC 10536 (K 2124) Inoculum $1,07 \times 10^9$ KBE / ml	
		1 Minute RF	5 Minuten RF	1 Minute RF	5 Minuten RF
Vergleichs-rezeptur	0,1	0,04	>4,87	3,69	>5,3
	0,3	0,59	>4,87	>5,2	>5,3
Rezeptur 1	0,1	3,42	>4,87	>5,2	>5,3
	0,3	>4,9	>4,87	>5,2	>5,3
Rezeptur 2	0,1	0	0,09	1,17	>5,3
	0,3	0,03	>4,87	>5,2	>5,3
Rezeptur 3	0,1	>4,9	>4,87	>5,2	>5,3
	0,3	>4,9	>4,87	>5,2	>5,3
Rezeptur 4	0,1	3,04	>4,87	>5,2	>5,3
	0,3	>4,9	>4,87	>5,2	>5,3

AWK = Anwendungskonzentration

RF-Werte = Keimreduktion in LOG-Stufen

**Tabelle 3:** Ergebnistabelle zur fungiziden Wirksamkeit nach DVG

Produkt	[AWK] %	Saccharomyces cerevisiae ATCC 9763 (K 5011) Inoculum $1,36 \times 10^7$ KBE / ml		Aspergillus niger ATCC 16404 (K 7444) Inoculum $1,07 \times 10^9$ KBE / ml	
		5 Minuten RF	30 Minuten RF	5 Minuten RF	30 Minuten RF
Vergleichs- rezeptur	0,3	0,21	0,24	0	0
	1,0	0,24	1,1	0	0
Rezeptur 1	0,3	2,88	>3,19	0	0
	1,0	>3,18	>3,19	0	0,02
Rezeptur 2	0,3	0,55	>3,19	0	0,38
	1,0	>3,18	>3,19	0,22	0,85
Rezeptur 3	0,3	>3,18	>3,19	0,31	0,54
	1,0	>3,18	>3,19	1,56	4,02
Rezeptur 4	0,3	3,18	3,19	0,39	0,87
	1,0	3,18	3,19	1,34	>4,02

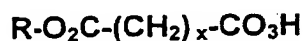
AWK = Anwendungskonzentration

RF-Werte = Keimreduktion in LOG-Stufen

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**P a t e n t a n s p r ü c h e**

1. Verwendung von Formulierungen, die mindestens eine Esterpersäure der allgemeinen Formel



worin R eine Alkylgruppe von 1 bis 4 Kohlenstoffatomen und x eine Zahl von 1 bis 4 ist,

enthalten,

zur Verbesserung der Oberflächenbenetzung bei Verwendung derartiger Formulierungen im Vergleich zur Verwendung gleicher molarer Mengen der entsprechenden Persäuren alleine oder in Kombination mit mol-äquivalenten Mengen des korrespondierenden Alkohols bei der Oberflächendesinfektion und/oder -reinigung.

2. Verwendung nach Anspruch 1, dadurch gekennzeichnet, daß auf nicht waagrecht angeordneten Oberflächen eine längere Kontaktzeit zur Oberfläche besteht, als bei Verwendung gleicher molarer Mengen der entsprechenden Persäuren alleine oder in Kombination mit mol-äquivalenten Mengen des korrespondierenden Alkohols.
3. Verwendung nach einem der Ansprüche 1 oder 2, dadurch gekennzeichnet, daß ein besserer antimikrobieller und/oder zusätzlicher Reinigungseffekt erzielt wird, als bei Verwendung gleicher molarer Mengen der entsprechenden Persäuren alleine oder in Kombination mit mol-äquivalenten Mengen des korrespondierenden Alkohols.
4. Verwendung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß es möglich ist, bei niedrigerer Konzentration und/oder reduzierter geruchlicher Belastung zumindest die gleiche antimikrobielle Wirksamkeit zu erreichen, wie bei Verwendung gleicher molarer Mengen der entsprechenden Persäuren al-

leine oder in Kombination mit mol-äquivalenten Mengen des korrespondierenden Alkohols.

5. Verwendung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß R eine Methylgruppe ist.
6. Verwendung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Formulierungen eine oder mehrere Esterpersäuren ausgewählt aus Per-succinsäuremonomethylester, Perglutarsäuremonomethylester, Peradipinsäuremonomethylester, Perbernsteinsäuremonomethylester enthalten.
7. Verwendung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß in der Formulierung 0,0001 bis 15 Gew.% einer oder mehrerer Esterpersäuren, bezogen auf die gesamte Formulierung, enthalten sind.
8. Verwendung nach Anspruch 7, dadurch gekennzeichnet, daß in der Formulierung 0,1 bis 5 Gew.% einer oder mehrerer Esterpersäuren, bezogen auf die gesamte Formulierung, enthalten sind.
9. Verwendung nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß in der Formulierung zusätzlich 1 bis 50 Gew.% Wasserstoffperoxid, bezogen auf die gesamte Formulierung, enthalten sind.
10. Verwendung nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß in der Formulierung zusätzlich 0,1 bis 25 Gew.% wenigstens einer nicht veresterten Persäure, bezogen auf die gesamte Formulierung, enthalten sind.
11. Verwendung nach Anspruch 10, dadurch gekennzeichnet, daß die in den Formulierungen vorliegenden nicht veresterten Persäuren ausgewählt sind aus Peressigsäure, Perpropionsäure, Persuccinsäure, Perglutarsäure, Peradipinsäure, Perbernsteinsäure,  $\omega$ -Phthalimidoperoxihexansäure, Perfettsäuren mit



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8 bis 18 Kohlenstoffatomen pro Molekül oder Mischungen der genannten Persäuren.

12. Verwendung nach einem der Ansprüche 1 bis 11, dadurch gekennzeichnet, daß in der Formulierung zusätzlich 5 bis 50 Gew.% wenigstens einer organischen Säure, bezogen auf die gesamte Formulierung, enthalten sind, die keine Persäure ist.
13. Verwendung nach Anspruch 12, dadurch gekennzeichnet, daß die in der Formulierung enthaltene organische Säure ausgewählt ist aus Essigsäure, Propionsäure, Succinsäure, Glutarsäure, Adipinsäure, Bernsteinsäure,  $\omega$ -Phthalimidoperoxihexansäure, Fettsäuren mit 8 bis 18 Kohlenstoffatomen pro Molekül oder aus Mischungen dieser Säuren.
14. Verwendung nach einem der Ansprüche 1 bis 13, dadurch gekennzeichnet, daß in der Formulierung zusätzlich wenigstens ein Hydrotrop enthalten ist.
15. Verwendung nach einem der Ansprüche 1 bis 14, dadurch gekennzeichnet, daß in der Formulierung zusätzlich wenigstens eine Komponente mit komplexierenden Eigenschaften für mehrwertige Metall-Ionen enthalten ist.
16. Verwendung nach einem der Ansprüche 13 bis 15, dadurch gekennzeichnet, daß in der Formulierung die Esterpersäure zusammen mit
  - a) wenigstens einer Fettsäure und/oder
  - b) wenigstens einem Hydrotrop und/oder
  - c) wenigstens einer tensidischen Schaumträgerkomponenteeine antimikrobielle synergistisch wirkende Zusammensetzung und/oder eine schaumbildende Kombination zur Reinigung und/oder Desinfektion von Oberflächen bilden.

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17. Verwendung nach Anspruch 16, dadurch gekennzeichnet, daß die tensidische Schaumträgerkomponente ein gegenüber Oxidationsmitteln stabiles Aminoxidderivat ist.
18. Verwendung nach einem der Ansprüche 1 bis 17, dadurch gekennzeichnet, daß die Formulierungen als wäßrige Lösung, Gel, Emulsion, Paste, Dispersion, Pulver, Granulat, Schuppen, Perlen, Tabletten, blockartige Formkörper, Extrudat vorliegen.
19. Verwendung nach einem der Ansprüche 1 bis 18, dadurch gekennzeichnet, daß die Formulierungen im Bedarfsfall vor dem Einsatz für Reinigungs- und/oder Desinfektionszwecke mit Wasser verdünnt werden.
20. Verwendung nach Anspruch 19, dadurch gekennzeichnet, daß der Verdünnungsfaktor zwischen 10 und 10000 liegt.
21. Verwendung nach einem der Ansprüche 1 bis 20, dadurch gekennzeichnet, daß die zu behandelnde Oberfläche durch Tauchen und / oder über Hilfsmittel, die ausgewählt sein können aus Pinsel, Schwamm, Rollen, Tücher, Lappen, Bürsten, Wischer, Gummi, Mops, Flachwischbezüge, Sprühvorrichtung behandelt wird.
22. Verwendung von Formulierungen gemäß den Ansprüchen 1 bis 21 als kombinierte Reinigungs- und Desinfektionsmittel.
23. Verwendung nach einem der Ansprüche 1 bis 22 zur Desinfektion von Mehrweg- und Einweggebinden aus Glas, Karton und/oder Kunststoff.
24. Verwendung nach einem der Ansprüche 1 bis 23 im Verfahrensablauf der aseptischen oder keimarmen Abfüllung von mikrobiologisch sensiblen Lebensmitteln.

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25. Verwendung nach Anspruch 24, dadurch gekennzeichnet, daß die Verpackungen vor der Abfüllung der mikrobiologisch sensiblen Produkte mit Formulierungen gemäß den Ansprüchen 1 bis 23 behandelt werden.
26. Verwendung nach Anspruch 24, dadurch gekennzeichnet, daß die im Bereich der keimarmen Abfüllung befindlichen Oberflächen, inklusive der lebensmitteiführenden Leitungen, Tanks, Geräte, Maschinen, Transportbändern und -anlagen, Rinser, Herstellvorrichtungen für die Gebinde mit Formulierungen gemäß den Ansprüchen 1 bis 23 behandelt werden.
27. Antimikrobielle synergistisch wirkende Zusammensetzung zur Reinigung und Desinfektion von Oberflächen, die mindestens eine Esterpersäure der allgemeinen Formel



worin R eine Alkylgruppe von 1 bis 4 Kohlenstoffatomen und x eine Zahl von 1 bis 4 ist, kombiniert mit einer Komponente, die ausgewählt ist aus

- a) wenigstens einer Fettsäure mit 8 bis 18 Kohlenstoffatomen und/oder
  - b) wenigstens einem Hydrotrop und/oder
  - c) wenigstens einer tensidischen Schaumträgerkomponente
- enthält.

28. Antimikrobielle synergistisch wirkende Zusammensetzung nach Anspruch 27, dadurch gekennzeichnet, daß die Fettsäure a) 8 bis 12 Kohlenstoffatome im Molekül enthält.
29. Zusammensetzung nach einem der Ansprüche 27 bis 28 dadurch gekennzeichnet, daß die tensidische Schaumträgerkomponente c) ein gegenüber Oxidationsmitteln stabiles Aminoxidderivat ist.

30. Zusammensetzung nach einem der Ansprüche 27. bis 29, dadurch gekennzeichnet, daß bezogen auf die gesamte Formulierung, 0,0001 bis 15 Gew.% einer Esterpersäure sowie

- a) 0,01 bis 15 Gew.% wenigstens einer Fettsäure mit 8 bis 18 Kohlenstoffatomen und/oder
- b) 0,01 bis 25 Gew.% wenigstens eines Hydrotrops und/oder
- c) 0,01 bis 15 Gew.% wenigstens einer tensidischen Schaumträgerkomponente

enthalten sind.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
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(19) Weltorganisation für geistiges Eigentum  
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25/30, C11D 3/48, A61L 2/18 // (A01N 37/16, 59:00,  
37:16, 37:04, 37:02), A61L 101:32, 101:36

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(81) Bestimmungsstaat (*national*): US.

(26) Veröffentlichungssprache: Deutsch

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Veröffentlicht:  
— mit internationalem Recherchenbericht

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(88) Veröffentlichungsdatum des internationalen  
Recherchenberichts: 16. Mai 2002

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Zur Erklärung der Zweibuchstaben-Codes und der anderen  
Abkürzungen wird auf die Erklärungen ("Guidance Notes on  
Codes and Abbreviations") am Anfang jeder regulären Ausgabe  
der PCT-Gazette verwiesen.

WO 01/47359 A3

(54) Title: PEROXY ACIDS WITH EXCELLENT ADHESION TO SURFACES

(54) Bezeichnung: PERSÄUREN MIT GUTER HAFTUNG AUF OBERFLÄCHEN

(57) Abstract: The invention relates to the use of ester peroxy acids for improving surface perfusion during the disinfection of surfaces and to synergistic antimicrobial combinations of ester peroxy acids and additional constituents.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft die Verwendung von Esterpersäuren zur Verbesserung der Oberflächenbenetzung bei der Desinfektion von Oberflächen sowie synergistische antimikrobielle Kombinationen von Esterpersäuren mit weiteren Komponenten.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/12689

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N37/16 A01N25/30 C11D3/48 A61L2/18 //(A01N37/16,  
59:00,37:16,37:04,37:02),A61L101:22,A61L101:36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N C11D A61L C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 765 309 A (SOLVAY INTEROX LTD) 2 April 1997 (1997-04-02) cited in the application the whole document	1-9,12, 14-27, 29,30
X	LION C ET AL: "Nouveaux décontaminants. Action des peracides à groupe ester sur quelques toxiques insecticides ou de guerre" BULLETIN DES SOCIETES CHIMIQUES BELGES,XX,XX, vol. 100, no. 7, 1991, pages 555-560, XP002086235 ISSN: 0037-9646 page 555	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*Z\* document member of the same patent family

Date of the actual completion of the international search

15 June 2001

Date of mailing of the international search report

25/06/2001

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## INTERNATIONAL SEARCH REPORT

Int. J. Application No

PCT/EP 00/12689

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 19287 A (SOLVAY INTEROX LTD) 12 November 1992 (1992-11-12)  abstract page 4, line 9-30 page 5, line 1-15 page 7, line 14-24 page 8, line 28-37	1, 10-13, 15, 18, 19, 21, 22
A	DE 196 39 603 A (HENKEL KGAA) 2 April 1998 (1998-04-02)  abstract page 6	1, 10-12, 15, 18, 19, 21, 22
A	US 5 200 189 A (KELLER JEROME D ET AL) 6 April 1993 (1993-04-06) abstract column 2 column 7	1, 14, 18, 21-26
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Information on patent family members

International Application No

PCT/EP 00/12689

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			SE 440846 B	26-08-1985



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### Information on patent family members

Inte .onal Application No

PCT/EP 00/12689

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# INTERNATIONALER RECHERCHENBERICHT

Int. Nationales Aktenzeichen

PCT/EP 00/12689

## A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES

IPK 7 A01N37/16 A01N25/30 C11D3/48 A61L2/18 //(A01N37/16, 59:00,37:16,37:04,37:02),A61L101:22,A61L101:36.

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

## B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)

IPK 7 A01N C11D A61L C07C

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

EPO-Internal, WPI Data, PAJ

## C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	EP 0 765 309 A (SOLVAY INTEROX LTD) 2. April 1997 (1997-04-02) in der Anmeldung erwähnt das ganze Dokument	1-9,12, 14-27, 29,30
X	LION C ET AL: "Nouveaux décontaminants. Action des peracides à groupe ester sur quelques toxiques insecticides ou de guerre" BULLETIN DES SOCIETES CHIMIQUES BELGES,XX,XX, Bd. 100, Nr. 7, 1991, Seiten 555-560, XP002086235 ISSN: 0037-9646 Seite 555	1-6

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

\* Besondere Kategorien von angegebenen Veröffentlichungen :

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\*Z\* Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche

15. Juni 2001

Absendedatum des internationalen Recherchenberichts

25/06/2001

Name und Postanschrift der Internationalen Recherchenbehörde  
Europäisches Patentamt, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Bevollmächtigter Bediensteter

Böhm, I

## INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen

PCT/EP 00/12689

## C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	<p>WO 92 19287 A (SOLVAY INTEROX LTD) 12. November 1992 (1992-11-12)</p> <p>Zusammenfassung Seite 4, Zeile 9-30 Seite 5, Zeile 1-15 Seite 7, Zeile 14-24 Seite 8, Zeile 28-37</p> <p>----</p>	<p>1,10-13, 15,18, 19,21,22</p>
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A	<p>US 5 200 189 A (KELLER JEROME D ET AL) 6. April 1993 (1993-04-06)</p> <p>Zusammenfassung Spalte 2 Spalte 7</p> <p>----</p>	<p>1,14,18, 21-26</p>
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Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internationales Aktenzeichen

PCT/EP 00/12689

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		WO 9301716 A	04-02-1993
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		NO 774045 A,B,	14-07-1978
		SE 440846 B	26-08-1985

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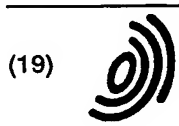
Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internationales Aktenzeichen

PCT/EP 00/12689

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
GB 1566671 A		SE 7714473 A	14-07-1978





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 0 967 203 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
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(51) Int. Cl.<sup>6</sup>: **C07C 409/24**, **C07C 407/00**,  
**A01N 37/16**

(21) Application number: **98304892.7**

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(54) **Process for the production of an aqueous monoester peroxy-carboxylic acid solution, the solution obtainable by this process, and its use as disinfectant**

(57) Process for the production of an aqueous monoester peroxy-carboxylic acid solution by reaction of a peroxygen compound with at least one dicarboxylic acid and with at least one alcohol optionally in the presence of an acid catalyst. Aqueous monoester peroxy-carboxylic acid solution obtainable by this process. Use of the aqueous monoester peroxy-carboxylic acid solution as disinfectant.

**EP 0 967 203 A1**

## Description

[0001] The present invention is related to a process for the production of an aqueous monoester peroxy-carboxylic acid solution. It also concerns the aqueous monoester peroxy-carboxylic acid solution obtainable by this process and its use in disinfectant compositions.

[0002] Compositions containing monoester percarboxylic acids and their preparation by reaction between a monoester of an aliphatic dicarboxylic acid and hydrogen peroxide have been described in the international patent application WO 95/34537 to SOLVAY INTEROX LIMITED. Such compositions were shown to have no discernible odour and to be effective as microbicide. Although the compositions exhibited a level of available oxygen stability that would enable them to remain effective during several months storage, there is a continuing need to find new solutions of monoester percarboxylic acids.

[0003] It is an object of the invention to provide a new or alternative process for the production of monoester peroxy-carboxylic acid solutions as well as to provide new monoester peroxy-carboxylic acid solutions.

[0004] Consequently, the present invention concerns a process for the production of an aqueous monoester peroxy-carboxylic acid solution by reaction of a peroxygen compound with at least one polycarboxylic acid and with at least one alcohol optionally in the presence of an acid catalyst. Preferably, the polycarboxylic acid is a dicarboxylic acid. While focused on this preferred embodiment the present invention is however not limited thereto.

[0005] One of the essential characteristics of the process of the invention resides in the nature of the starting materials especially the dicarboxylic acid and the alcohol which render the process particularly performing. Indeed, by using these starting materials new solutions can be produced. It will be recognised that a complex mixture will be obtained using the process according to the invention containing the desired monoester peroxy-carboxylic acid (called ester peracid hereafter), water, and may also contain residual amounts of non consumed dicarboxylic acid (called diacid hereafter), peroxygen compound, alcohol and optional acid catalyst, and in situ generated corresponding diester, monoester carboxylic acid, monocarboxylic peroxy-carboxylic acid and diperoxy-carboxylic acid. The advantage of the process of the invention resides in the possibility to control the relative amounts of the desired ester peracid to all the other products generated in situ. Indeed, by varying the amount of alcohol in the reaction mixture, more or less of the ester peracid will be produced relative to the amount of other products. So, a large variety of solutions can be obtained using a single process.

[0006] Another advantage resulting from the nature of the starting materials resides in the duration of the process. Indeed, the diacids used as starting material in the present invention have generally a higher solubility in

the reaction mixture than have monoesters of dicarboxylic acids which are used in the known process described in the international patent application WO 95/34537. The higher solubility results in faster dissolution rates and thus shorter production times.

[0007] Yet another advantage of the process of the invention resides in the availability of the starting materials. Indeed, diacids and alcohols are more readily available than monoesters of a dicarboxylic acid.

[0008] Yet another advantage of the process of the present invention resides in the large choice of the organic radical of the ester group. Indeed, in the known process of the international patent application WO 95/34537 the choice of the organic radical of the ester group is determined by the choice of the monoester of a dicarboxylic acid used as starting material whereas in the present invention the organic radical of the ester group originates from the alcohol. It is clear that in the process of the invention alcohols can be used which are not available as monoesters.

[0009] The diacid used in the process of the invention can be chosen from any compound containing at least two carboxylic acid groups and which is capable of being transformed in an ester peracid in the process of the invention. The diacid can contain up to 20 carbon atoms, preferably up to 10 carbon atoms. The principal chain of the diacid which is substituted by the two carboxylic groups can be linear, branched, cyclic or aromatic, optionally unsaturated and/or containing a heteroatom. Oxalic acid is convenient. Diacids with a linear principal chain generally corresponding to the formula  $\text{COOH} \cdot \text{R} \cdot \text{COOH}$  in which R is an alkylene group containing up to 6 carbon atoms can also be used. Suitable examples are adipic acid, glutaric acid and succinic acid. Examples of diacids with a branched principal chain are methyl succinic and ethyl malonic acids. Other examples are maleic, fumaric and malic acids. The preferred diacids are adipic, glutaric and succinic acids. A mixture of two or more different diacids can be used in the process of the invention.

[0010] The diacid is generally used in an amount of at least 0,05 % wt of the reaction mixture, preferably at least 5 % wt. The amount of diacid used is usually at most 65 % wt, in particular at most 25 % wt. Quantities from 0,05 to 65 % wt of diacid are convenient.

[0011] The peroxygen compound used in the process according to the invention can be chosen from hydrogen peroxide or any other peroxygen compound capable of releasing hydrogen peroxide in the reaction mixture of the process of the present invention. The expression "reaction mixture of the process of the invention" means a mixture containing water, the diacid, the alcohol, the peroxygen compound, optionally the acid catalyst, the ester peracid, the corresponding diester, monoester carboxylic acid, monocarboxylic peroxy-carboxylic acid and diperoxy-carboxylic acid. In particular, the peroxygen compound can be chosen from hydrogen peroxide, inorganic peracids, organic peracids and persalts. An



example of inorganic peracid is Caro's acid. Organic acids containing up to 10 carbon atoms are convenient. An example of such an organic peracid is peracetic acid. Examples of persalts are sodium percarbonate and sodium perborate mono- or tetrahydrate. Hydrogen peroxide is preferred.

[0012] The peroxygen compound is generally used in an amount of at least 0,01 % wt of the reaction mixture, in particular at least 5 % wt. The amount of peroxygen compound used is usually at most 30 % wt of the reaction mixture, preferably at most 25 % wt. Quantities of peroxygen compound from 0,05 to 30 % wt are convenient. When hydrogen peroxide is used, it can be added to the reaction mixture in the form of an aqueous solution containing from 1 to 85 % wt of hydrogen peroxide. The molar ratio of the peroxygen compound to the diacid can be varied in a wide range. Generally this molar ratio is at least 0,1 : 1, preferably at least 1 : 1. The molar ratio is usually at most 35 : 1, in particular at most 7 : 1.

[0013] The alcohol used in the process of the invention can be chosen from any compound containing at least one hydroxyl group. Monoalcohols containing up to 20 carbon atoms are suitable, those containing up to 10 carbon atoms are preferred. Examples of suitable monoalcohols are methanol and ethanol. Diols containing up to 20 carbon atoms, preferably up to 10 carbon atoms can also be used. Examples of suitable diols are ethylene glycol and propylene glycol. Polyols containing up to 20 carbon atoms can also be used. Examples of suitable polyols include sorbitol and mannitol. Alcohol ethoxylates could also be used. A mixture of two or more different alcohols can be used in the process of the invention.

[0014] The alcohol is generally used in an amount of at least 0,01 % wt of the reaction mixture, in particular of at least 2 % wt. The amount of alcohol used is usually at most 45 % wt, more particularly at most 25 % wt. Quantities of alcohol from 0,05 to 45 % wt are convenient. The molar ratio of the alcohol to the diacid can be varied within a wide range. Generally the ratio is at least 0,1 : 1, preferably at least 0,5 : 1. The molar ratio is usually at most 10 : 1, in particular at most 1 : 1.

[0015] The acid catalyst optionally used in the process of the invention can be an inorganic or organic acid having a pKa of about 3 or lower, and preferably having a pKa of below 1. It is particularly desirable to employ a non-halide mineral acid such as sulphuric or phosphoric or sulphamic acid or an organic sulphonic acid such as methyl or toluene sulphonic acid or a cation exchange resin doped with acid. Organic acids can also be used. Those containing up to 10 carbon atoms are convenient. An example of organic acid is citric acid.

[0016] The catalyst is desirably used in a concentration of at least 0,05 % wt in the reaction mixture, in particular at least 0,1 % wt. The acid catalyst concentration is in many instances at most 10 % wt, especially at most 2,5 % wt. Quantities of acid catalyst from 0,05 to 10 %

wt are convenient.

[0017] The invention process can be carried out at ambient temperature or at an elevated temperature. In practice the temperature can be at least 10°C, in particular at least 15 °C. When it is desirable to achieve equilibration rapidly temperatures of at least 30 °C can be used. The temperature is commonly at most 60 °C, especially at most 30 °C.

[0018] The duration of the invention process can vary within a very wide range and depends on whether it is desired to obtain an equilibrium solution or a non-equilibrium solution. Equilibration can already be reached after a duration of at least 5 mm. The duration is commonly at most 24 h.

[0019] The invention process can be carried out in any apparatus adequate for mixing the starting materials (diacid, peroxygen compound, alcohol, water and acid catalyst).

[0020] According to the process of the invention the starting materials (diacid, peroxygen compound, alcohol, water and acid catalyst) can be added in any order.

[0021] The reaction mixture can be stirred during the process of the invention.

[0022] The process of the invention is very useful for producing aqueous monoester peroxycarboxylic acid solutions containing the monoester peroxycarboxylic acid, water, residual amounts of non consumed peroxygen compound, dicarboxylic acid, alcohol and optional acid catalyst, and in situ generated corresponding diester, monoester carboxylic acid, monocarboxylic peroxycarboxylic acid and diperoxycarboxylic acid.

[0023] Consequently, the present invention also concerns aqueous monoester peroxycarboxylic acid solutions obtainable by the process described above containing the ester peracid, water, residual amounts of non consumed peroxygen compound, one or more diacids, one or more alcohols and optional acid catalyst, and in situ generated corresponding diester, monoester carboxylic acid, monocarboxylic peroxycarboxylic acid and diperoxycarboxylic acid. Particularly beneficial solutions are those obtainable by the process wherein the amounts of alcohol and diacid used are such that the molar ratio of hydroxy groups present in the alcohol to the carboxylic acid groups present in the diacid is different from 1.

[0024] The pH of the invention solutions can vary in a wide range. The pH is generally at least -2, most often at least 1. pH values of at most 8 are possible, values of at most 5 are preferred.

[0025] The concentration of ester peracid in the solution of the invention is generally at least 0,001 % wt, in particular at least 0,005 % wt. The ester peracid concentration is usually at most 35 % wt, especially at most 5 % wt.

[0026] The amount of water present in the solution of the invention can vary within a very wide range since the solutions can be very dilute or very concentrated. The water content is commonly at least 10 % wt. The

amount of water is often at most 90% wt.

[0027] The solution of the invention contains in many cases residual amounts of non consumed peroxygen compound from 0,1 to 30 % wt.

[0028] The diacid is usually present in the solution of the invention in a residual amount of at least 0,05% wt. The amount of diacid is commonly at most 10 % wt. The solution of the invention can contain a mixture of two or more different diacids.

[0029] If residual amounts of alcohol are found in the solution of the invention, these amounts are commonly at least 0,1 % wt. The amount of alcohol is often at most 10 % wt. The solution of the invention can contain a mixture of two or more different alcohols.

[0030] The residual amount of optional acid catalyst that can be present in the solution of the invention is usually from 0 to 5 % wt.

[0031] The solution of the invention can contain an amount of in situ generated diester from 0 to 5 % wt.

[0032] The in situ generated monoester carboxylic acid can be present in the solution of the invention in an amount from 0 to 10 % wt.

[0033] The concentration of in situ generated monocarboxylic peroxy-carboxylic acid that can be found in the solution of the invention is often from 0 to 30 % wt.

[0034] The amount of in situ generated diperoxy-carboxylic acid that can be present in the solution of the invention is commonly from 0 to 10 % wt.

[0035] Particularly beneficial solutions are those containing at least 0,01 % wt of monoester peroxy-carboxylic acid, at least 0,1 % wt of peroxygen compound, at least 0,05% wt of dicarboxylic acid and at least 0,1 % wt of alcohol.

[0036] The solution of the invention can contain other additives. These additives can be chosen from stabilisers, surfactants and thickeners. Such additives are often incorporated in an amount from 0,02 to 20 %, and in many instances from 0,1 to 10 % wt of the solution.

[0037] Suitable stabilisers include hydroxy substituted aromatic carboxylic acids and ester derivatives thereof, particularly phenol carboxylic acids such as p-hydroxybenzoic acid and ester derivatives such as methyl or ethyl esters. They also include organic polyphosphonic acid sequestrants such as ethyldiene diphosphonic acid, and aminopolymethylenephosphonic acids, pyridine carboxylic acids especially dipicolinic acid and mixtures thereof. In addition inorganic stabilisers may be used. An example of inorganic stabiliser is colloidal tin.

[0038] The surfactants can be nonionic, anionic or amphoteric. Surfactants can be soap or synthetic. Typical examples are described in chapter 2 of Synthetic Detergents by A. Davidson and B/M. Milwidsky, 6<sup>th</sup> Edition published in 1978 by George Godwin Limited. Cationic surfactants include quaternary ammonium salts, non-halide examples include sulphates, metosulphates, ethosulphates, hydroxides, acetates, saccharinates phosphates and propionates.

[0039] Typical examples of suitable non-surfactant

thickeners are cross linked polyacrylates, natural gums such as xanthan or rhamsan gum, cellulose derivatives such as carboxymethyl cellulose and silicates.

[0040] The solutions of the invention can also contain additional non-halide mineral acids. These acids can be selected from sulphuric, phosphoric or sulphamic acid or an organic sulphonic acid. The acid can be present at a concentration from 0,05 to 10 % wt in the solution.

[0041] Particularly desirable solutions are those containing up to 20 % wt of surfactant, from 0,025 to 5 % wt of stabiliser and from 0,05 to 10 % wt of a non-halide mineral acid.

[0042] The solution of the invention can be advantageously used as disinfectant. The present invention concerns therefore also the use of the above described solutions as disinfectants. The method for disinfection according to the present invention comprises contacting the substrate to be disinfected with the solution as a storage stable aqueous acidic solution of an ester peracid or prepared from one. The solution may be employed with or without dilution. When compositions are diluted, dilution is usually chosen to give an ester peracid concentration in solution of between about 1 part per million and 10000 parts per million, depending on the substrate. The disinfecting method can use a wide range of temperatures, typically from about 4 °C to the boiling point of the disinfectant. The solution of the invention can be used in a range of disinfection applications e.g. disinfection of micro-organism contaminated aqueous media e.g. process waters containing bacteria, algae, yeasts and viruses from industries such as paper and pulp, food processing e.g. sugar refining, brewing, wine making, discharges from sewage treatment works, meat processing factories, carcase rendering and livestock rearing. Other substrates include irrigation water in the horticultural industry, contaminated cooling waters, and contaminated surfaces in e.g. food processing, horticulture, catering, domestic or hospital environments. The invention compositions can be used to treat crops and harvested plants or plant products.

[0043] The solutions of the invention may be used for other purposes where peracids are used, including bleaching or as a bleach additive in washing processes.

[0044] Having described the invention in general terms, specific embodiments thereof are described in greater detail by way of example.

#### Example 1

[0045] A solution containing 14,04 g glutaric acid, 9,79 g ethanol, 17,65 g concentrated hydrogen peroxide (85,5 % wt), 1 g concentrated sulphuric acid, 57,52 g demineralised water, 0,1 g p-hydroxy benzoic acid, 0,17 g of 1-hydroxyethane-1,1-diphosphonic acid (Briquest ADPA 60A) was prepared with stirring, and allowed to reach equilibrium. The molar ratio of ester peracid to monocarboxylic peroxy-carboxylic acid found in the system was 1 :8, measured by HPLC.

Example 2

[0046] A solution was prepared by mixing and stirring 16,5 g glutaric acid, 8 g methanol, 17,65 g concentrated hydrogen peroxide (85 % wt), 0,1 g parahydroxy benzoic acid, 0,2 g Briquest ADPA 60A, 1 g concentrated sulphuric acid, 56,6 g water. The solution was allowed to reach equilibrium. The molar ratio of ester peracid to monocarboxylic peroxy-carboxylic acid found in the system was 1 :3.

Example 3

[0047] A solution was prepared as described in example 2 with a lower level of methanol, 3 g methanol instead of 8 g, a lower level of Briquest ADPA 60A, 0,17 g instead of 0,2 g, a higher level of water, 61,6 g instead of 56,6 g. The molar ratio of ester peracid to monocarboxylic peroxy-carboxylic acid found in the system was 1 :11.

Example 4

[0048] A solution was prepared by mixing and stirring 16,5 g of a mixture of adipic, glutaric and succinic acids, 8 g of methanol, 17,65 g concentrated hydrogen peroxide (85 % wt), 1 g concentrated sulphuric acid, 56,6 g demineralised water, stabilised with 0,1 g para-hydroxybenzoic acid and 0,17 g Briquest ADPA 60A. The solution was allowed to reach equilibrium. The presence of esters peracids was detected by HPLC.

Claims

1. Process for the production of an aqueous monoester peroxy-carboxylic acid solution by reaction of a peroxygen compound with at least one polycarboxylic acid and with at least one alcohol optionally in the presence of an acid catalyst.
2. Process according to claim 1, wherein the polycarboxylic acid is a dicarboxylic acid containing up to 20 carbon atoms, and wherein the dicarboxylic acid is used in an amount from 0,05 to 65 % wt.
3. Process according to claim 1 or 2, wherein the peroxygen compound is chosen from hydrogen peroxide, inorganic peracids, organic peracids, persalts, wherein the peroxygen compound is used in an amount of 0,05 to 30 % wt of the reaction mixture.
4. Process according to any one of claims 1 to 3, wherein the alcohol is chosen from monoalcohols, dialcohols and polyols containing up to 20 carbon atoms, wherein the alcohol is used in an amount from 0,05 to 45 % wt of the reaction mixture and wherein the molar ratio of alcohol to dicarboxylic acid is from 0,1 :1 to 10 :1.
5. Process according to any one of claims 1 to 4, wherein an acid catalyst is used chosen from inorganic or organic acids having a Pka of 3 or lower, wherein the acid catalyst is used in an amount from 0,05 to 10 % wt of the reaction mixture.
6. Aqueous monoester peroxy-carboxylic acid solution obtainable by the process of any of the preceding claims containing the monoester peroxy-carboxylic acid, water, residual amounts of non consumed peroxygen compound, one or more dicarboxylic acids, one or more alcohols and optional acid catalyst, and in situ generated corresponding diester, monoester carboxylic acid, monocarboxylic peroxy-carboxylic acid and diperoxy-carboxylic acid.
7. Aqueous monoester peroxy-carboxylic acid solution according to claim 6 wherein the amounts of alcohol and dicarboxylic acid used in the process are such that the molar ratio of hydroxy groups present in the alcohol to the carboxylic acid groups present in the dicarboxylic acid is different from 1.
8. Aqueous monoester peroxy-carboxylic acid solution according to claims 6 or 7 containing at least 0,01 % wt of monoester peroxy-carboxylic acid, at least 0,1 % wt of peroxygen compound, at least 0,05 % wt of dicarboxylic acid, at least 0,1 % wt of alcohol.
9. Aqueous monoester peroxy-carboxylic acid solution according to any one of claims 6 to 8 containing additionally up to 20 % wt of surfactant, from 0,025 to 5 % wt of stabiliser and from 0,05 to 10 % wt of a non-halide mineral acid.
10. Use of the aqueous monoester peroxy-carboxylic acid solution of any one of claims 6 to 8 as disinfectant.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 4892

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 November 1998	Examiner Bonnevalle, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate documents</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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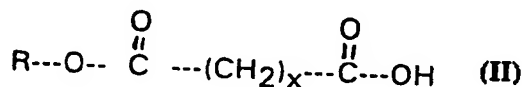
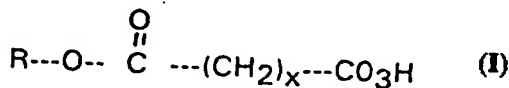
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(74) Agent: PEARCE, Timothy; Solvay Interlox Limited, Patent Dept., P.O. Box 51, Moorfield Road, Widnes WA8 0FE (GB).			

(54) Title: PEROXYGEN COMPOSITIONS



(57) Abstract

Storage stable, aqueous acidic solutions having a pH in the range of from 1 to 5 comprising at least one ester peracid having general formula (I), where R represents an alkyl group having from 1 to 4 carbons and x equals 1 to 4 are provided. The solutions can be prepared by contacting an aqueous solution of a carboxylic compound having general formula (II), where x is from 1 to 4 and R represents an alkyl group having from 1 to 4 carbons with an inorganic peroxygen compound, preferably hydrogen peroxide, at a pH of less than 4 until at least some ester peracid is produced, and thereafter adjusting the pH to be in the range of from 1 to 5, if necessary.

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<p>(21) International Application Number: <b>PCT/GB95/01398</b></p> <p>(22) International Filing Date: <b>15 June 1995 (15.06.95)</b></p> <p>(30) Priority Data: 9412051.6                      16 June 1994 (16.06.94)                      <b>GB</b></p> <p>(71) Applicant (for all designated States except US): <b>SOLVAY INTEROX LIMITED [GB/GB]; Baronet Works, Baronet Road, Warrington, Cheshire WA4 6HB (GB).</b></p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): <b>CARR, Graham [GB/GB]; 5 Bishop's Court, Woolton, Liverpool L25 5HR (GB). JAMES, Alun, Pryce [GB/GB]; 28 Dowhills Road, Blundellsands, Liverpool L23 8SW (GB).</b></p> <p>(74) Agent: <b>PEARCE, Timothy; Solvay Interlox Limited, Patent Dept., P.O. Box 51, Moorfield Road, Widnes WA8 0FE (GB).</b></p>	<p>(81) Designated States: <b>AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).</b></p> <p><b>Published</b> <i>With international search report.</i></p>	
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$\text{R---O---}\overset{\text{O}}{\parallel}\text{C---}(\text{CH}_2)_x\text{---CO}_3\text{H} \quad \text{(I)}$ $\text{R---O---}\overset{\text{O}}{\parallel}\text{C---}(\text{CH}_2)_x\text{---}\overset{\text{O}}{\parallel}\text{C---OH} \quad \text{(II)}$		
<p>(57) Abstract</p> <p>Storage stable, aqueous acidic solutions having a pH in the range of from 1 to 5 comprising at least one ester peracid having general formula (I), where R represents an alkyl group having from 1 to 4 carbons and x equals 1 to 4 are provided. The solutions can be prepared by contacting an aqueous solution of a carboxylic compound having general formula (II), where x is from 1 to 4 and R represents an alkyl group having from 1 to 4 carbons with an inorganic peroxygen compound, preferably hydrogen peroxide, at a pH of less than 4 until at least some ester peracid is produced, and thereafter adjusting the pH to be in the range of from 1 to 5, if necessary.</p>		

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### Peroxygen Compositions

This invention concerns peroxygen compositions. More specifically, this invention concerns solutions of peracids, and still more specifically, this invention concerns solutions of ester peracids.

15 It is well known that certain classes of compound exert a very strong microbicidal effect which renders them suitable for use as disinfectants in a wide range of applications, especially domestic and industrial hard surface disinfection. One of the most commonly employed compounds is sodium hypochlorite solution, because it is readily available at low cost and is  
20 reasonably effective as a disinfectant over short contact times. In recent years, however, there has been increasing concern expressed at the possible environmental consequences of the use of hypochlorite solutions, including the possible formation of chlorinated organic compounds, such as trihalomethanes, and so attempts have been made to identify alternative  
25 disinfectants.

One group of chemicals which it has hitherto been proposed to employ as an alternative to hypochlorite disinfectants comprises organic peroxygen compounds, particularly aliphatic C<sub>1</sub> to C<sub>3</sub> peracids such as peracetic acid. Although very effective microbicides, some people find the odour of these  
30 aliphatic peracids to be offensive or irritating, and so for applications in which the disinfectant is likely to be employed in the proximity of people, it is desirable to find alternative disinfectants.

Many disinfectant compositions, particularly household disinfectants employ a concentrated solution of disinfectant which is diluted to the required  
35 concentration in use. Many such concentrated solutions employ water as the solvent on account of its low cost, ready availability and ease of safe handling compared with organic solvents. It is obviously desirable that the disinfectant forms a single phase system in the concentrated solution because this avoids

the need for the solution to be agitated before use. The formation of a single phase system reduces the possibility of the disinfectant becoming unevenly distributed throughout the composition and hence the possibility of inadequate or excessive dosing of the disinfectant.

- 5 Ester peracids are known in the prior art. For example, European Patent application No. EP-A-0 166 571 teaches the use of ester peracids of the general formula  $[RX]_m AOOH$ , where R is hydrocarbyl or alkoxylated hydrocarbyl, X is a heteroatom moiety, preferably oxygen, A is a wide range of organic moieties containing one or two carbonyl groups and m is one or  
10 two, for use in bleaching and laundry applications.

European Patent application No. EP-A-0 426 217 teaches the use of ester peracids of the general formula  $X-O_2C-A-CO_3H$ , where A is a C1 to C12 alkyl, aryl or alkaryl radical and X is a C1 to C20 alkyl, aryl, alkyl aryl radical, optionally including a heteroatom, for use in bleaching and cleaning systems.

- 15 Both French Patent application no. 2324626 and a paper by Nedelec et al, Synthesis, 1976, pp821-3 teach a method for the preparation and isolation of ester peracids from the reaction between acid chlorides and hydrogen peroxide in organic solvents.

- A paper by C. Lion et al, Bull. Soc. Chim. Belg. 1991, 100, pp555-559  
20 discloses the preparation and isolation of ester peracids by the reaction between ester acid and hydrogen peroxide in the presence of high concentrations of sulphuric acid, and quenching into ice. The ester peracids so produced are employed in the destruction of toxic organophosphorus compounds in aqueous alkaline solution.

- 25 None of the prior art references specifically disclose the storage stable, aqueous acidic ester peracid solutions of the present invention, or the use of solutions of such ester peracids as disinfectants.

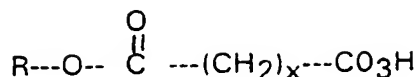
It is an objective of the present invention to provide novel storage stable, aqueous acidic ester peracid solutions.

- 30 It is another objective of the present invention to provide a peracid microbicide with reduced odour compared with C1 to C3 aliphatic peracids.

It is yet another objective of the present invention to provide a method for preparing storage stable, aqueous acidic ester peracid solutions.

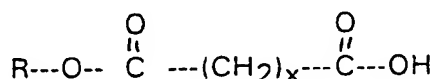
- It is a further objective of the present invention to provide a method for  
35 disinfecting using low odour peracids.

According to the present invention, there are provided storage stable, aqueous acidic solutions having an pH in the range of from 1 to 5 comprising at least one ester peracid having the general formula:



5 where R represents an alkyl group having from 1 to 4 carbons and x is from 1 to 4.

According to another aspect of the invention, there is provided a process for preparing storage stable, aqueous acidic solutions comprising at least one ester peracid, characterised in that the process comprises contacting  
 10 an aqueous solution of one or more carboxylic compounds having the general formula:

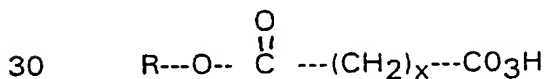


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where x is from 1 to 4, R represents an alkyl group having from 1 to 4 carbons and x is from 1 to 4 with an inorganic peroxygen compound at a pH of less than 4, preferably 3 or less, until at least some ester peracid has been produced and, thereafter, where the pH of the resultant ester peracid solution  
 20 produced is less than 1, its pH is adjusted to be in the range of from 1 to 5.

A further aspect of the invention provides a method for disinfecting characterised in that a substrate to be disinfected is contacted with a disinfectant prepared from a storage stable, aqueous acidic solution as hereinbefore defined.

25 The aqueous acidic solutions according to the present invention comprise at least one ester peracid defined by having the general chemical formula:



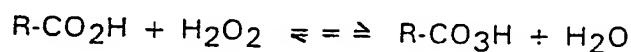
where R represents an alkyl group having from 1 to 4 carbons and x is from 1 to 4. When R has 3 or 4 carbons, the alkyl group can be linear or branched, i.e. the alkyl group can be n- or isopropyl, or n-, iso- or tertiary butyl.

35 Preferably, R is a methyl group. In many cases, the value of x is 2, 3 or 4.

In a particular embodiment, the solution according to the present invention comprises a mixture of the ester peracids where x is 2, 3 and 4, i.e. a mixture of the monoesters of peradipic, perglutaric and persuccinic acids. In

a particularly preferred embodiment, the major fraction of the ester peracids present in the composition has x equal to 3.

The solutions according to the present invention have a pH in the range of from 1 to 5, and preferably from 1.5 to 4. In certain embodiments, the pH of the solutions is greater than 1.75, and may be greater than 2, for example 2.5 or more. A pH in the range of from 3 to 3.5 may be advantageous in certain embodiments. The ester peracid solutions according to the present invention can often exist as equilibrium mixtures in aqueous solution, in which the ester peracid is in equilibrium with water, hydrogen peroxide and the non-peroxidised acid. The equilibrium obeys the following general equation:



where R represents hydrogen or an organic radical. It will be readily apparent that, for a fixed concentration of one component, the relative concentrations of the individual components can vary over a wide range and still be at equilibrium. When a solution of an ester peracid is not at equilibrium, chemical reaction takes place such that the composition of the mixture changes towards that of the equilibrium composition.

The solutions according to the present invention have the advantage of storage stability, ie the activity of the ester peracid component of the solution is retained through extended periods of storage. Depending on the application, the desired storage stability can range from periods of several days, for example 10 or more days, to periods of several, for example 4 or more, weeks, and even several, for example, 3 or more, months.

The ester peracids often present in the solutions, either in use or in storage, at a total concentration of from about 0.0001 to about 15% by weight of the solution, preferably from about 0.05 to about 10 % by weight, and more preferably from about 0.1 to about 5% by weight. It will be recognised that ester peracid solutions for storage and/or transportation, particularly where a dilution to produce an in use composition will be employed, will often comprise at least 0.1% by weight ester peracid, preferably at least 1% by weight ester peracid.

The total concentration of non-peroxidised ester acids is typically up to about 15% by weight of the solutions, although concentrations of up to 30% can be employed in certain embodiments, often from about 0.05 to about 10%, most often from about 1% to about 9%.

Hydrogen peroxide is typically present in the solutions at a concentration of up to 30% by weight, with concentrations in the range of from 15 to 25 %, for example about 20% by weight, giving particularly good results in certain embodiments. In other embodiments, the concentration of hydrogen peroxide is often from about 0.5 to about 15%, more often from about 1 to about 10%.

Optional components in solutions according to the present invention comprise stabilisers, inert inorganic salts, surfactants, dyes, perfumes, corrosion inhibitors and, where thickening is not achieved by a combination of components present for other purposes, thickeners. The optional components can be present at a wide range of concentrations, but in many cases, the total concentration of these optional components will not exceed 25% by weight.

Stabilisers can desirably be employed to improve the storage stability of solutions according to the invention and are especially desirable where the proposed application involves the likely chance that the ester peracid will be contacted with compounds known to cause decomposition, for example transition metal ions. Suitable chelating agents are often aminopolycarboxylic acids or salts thereof such as EDTA or DTPA, and/or carboxylic acid substituted N-containing heterocyclics, such as 8-hydroxyquinoline or picolinic or dipicolinic acid, and organopolyphosphonates, including hydroxyethylidenediphosphonic acid, and alkyleneaminomethylene phosphonic acids such as ethylene diaminetetra methylene phosphonic acid, cyclohexane-1,2-diaminetetramethylene phosphonic acid and diethylenetriaminepenta methylene phosphonic acid. A combination of an organophosphonate and an N-heterocyclic carboxylic acid is particularly suitable. The amount of chelant in the solution is at the discretion of the formulator, but is preferably greater than 0.25% and often not greater than about 1.5%, calculated as active material therein.

The surfactants which can be employed herein can be nonionic, anionic, cationic, or amphoteric. Generally, the surfactants contain at least one hydrophobic group, e.g. an aliphatic hydrocarbon group containing at least 8 carbon atoms, and often from 10 to 26 carbon atoms, the aliphatic group often being acyclic, but sometimes containing an alicyclic group, or the hydrophobic group can be an alkaryl group containing at least 6 and preferably up to 18 aliphatic carbon atoms. The surfactant contains in addition at least one water-solubilising group for example a sulphonate, sulphate, or carboxylic group which is linked either directly or indirectly to the hydrophobic group. Linking members can include residues of polyhydric alcohols containing etheric

- or esteric linkages, for example derived from ethylene glycol, propylene glycol, glycerine or polyether residues. The surfactants can be soap or be synthetic, for example as described in chapter 2 of synthetic Detergents by A. Davidsohn and B. M. Milwidsky, 6th Edition published in 1978 by George Godwin
- 5 Limited, and methods of making them are described in chapter 5 of the same book. Amongst anionic surfactants described on pages 11-23 of the aforementioned book, sulphonates and sulphates are of special practical importance. The sulphonates include, for example, alkaryl sulphonates, and particularly alkyl benzene sulphonates, the alkyl group preferably being a
- 10 straight chain containing 9 to 15 carbon atoms, of which one of the most commonly employed surfactants is linear dodecyl benzene sulphonate. Other anionic sulphonates which are useful in solutions herein include olefin sulphonates, obtained, for example, by sulphonating primary or secondary aliphatic mono-olefins, alkane sulphonates, especially linear alkane
- 15 sulphonates, and hydroxy alkane sulphonates and disulphonates, especially 3-, 4-, and 5-hydroxy-n-alkyl sulphonates in which the alkyl group contains any even number from 10 to 24 carbon atoms. Other desirable anionic surfactants include alcohol sulphates, preferably linear, having a chain length of at least 10 carbon atoms and sulphated fatty acid alkanolamides. Other sulphates
- 20 comprise sulphated nonionic surfactants as for example alkylphenoxyethylene oxide ether sulphate in which the alkyl groups contain from about 8 to 12 carbon atoms and there are 1 to 10 units of ethylene oxide in each molecule. Yet other sulphate surfactants comprise alkyl ether sulphates where the alkyl group contains from 10 to 20 carbon atoms, preferably linearly and each
- 25 molecule contains from 1 to 10 preferably from 1 to 4 molecules or ethylene oxide. Further anionic surfactants include phosphate derivatives of the ethylene oxide based nonionic surfactants described herein.

It is of considerable advantage that at least a proportion of the anionic surfactant be in liquid form or readily liquifiable.

- 30 In many suitable classes of anionic surfactants the counter ion is a monovalent metal ion, often a sodium or potassium ion, or a quaternary ammonium cation derived for example from ethanolamine or isopropylamine.

- In practice, cationic detergents are normally not present in the same composition as anionic surfactants, but when cationic detergents are used they
- 35 are frequently quaternary ammonium salts such as tetraalkyl ammonium salts in which at least one of the alkyl group contains at least 10 carbon atoms or quaternary pyridinium salts substituted by an alkyl chain of at least 10 carbon atoms. Although quaternary ammonium halides, commonly chlorides, can be



employed, particularly where the quaternary ammonium halide and ester peracid are combined shortly before use, in many embodiments it is preferred to employ non-halide quaternary ammonium salts. The use of non-halide quaternary ammonium salts is particularly preferred where the solution containing the ester peracid and quaternary ammonium salt are to be stored for any significant period. The use of quaternary ammonium halides in such solutions for storage can cause decomposition of the ester peracid by oxidation of the halide. Examples of non-halide quaternary ammonium salts include sulphates, methosulphates, ethosulphates, hydroxides, acetates, saccharinates, phosphates and propionates.

10 A considerable proportion of nonionic surfactants suitable for use in the present invention comprises condensation products of ethylene oxide and possibly propylene oxide. One class of such nonionic surfactants which is of special importance comprises water soluble condensation products of alcohols containing from 8 to 18 carbon atoms with an ethylene oxide polymer often  
15 containing at least 5 moles of ethylene oxide per molecule of surfactants, e.g. from 7 to 20 moles of ethylene oxide. Other nonionic surfactants comprise water soluble condensates of alkyl phenols or alkyl naphthols with an ethylene oxide polymer normally containing from 5 to 25 moles of ethylene oxide per mole of alkyl phenol or alkyl naphthol. The alkyl group normally contains from  
20 6 to 12 carbon atoms and is frequently linear. As an alternative to the hydrophobic moiety of the nonionic surfactant being linked to the hydrophilic moiety by an ether link as in alcohol or phenol/ethylene oxide condensates, the linkage can be an ester group. The hydrophobic moiety is normally the residue of a straight chain aliphatic acid containing from 8 to 22 carbon atoms and  
25 more particularly lauric, stearic and oleic residues. In one class of nonionic ester surfactants, the hydrophilic moiety often comprises polyethylene oxide, frequently in the ratio of from 5 to 30 moles of ethylene oxide per mole of the fatty acid residue. It will be recognised that both mono and di esters can be employed. Alternatively it is possible to employ as the hydrophilic moiety  
30 glycerol, thereby producing either mono or di glycerides. In a further group, the hydrophilic moiety comprises sorbitol. A further class of nonionic surfactants comprise alkanolamides which can be obtained when a C10 to C22 amide is condensed with a polyethylene oxide or polypropylene glycol hydrophilic moiety or moieties. Semi-polar detergents include water soluble  
35 amine oxides, water soluble phosphine oxides and water soluble sulphur oxides, each containing one alkyl moiety of from 10 to 22 carbon atoms and two short chain moieties selected from the groups of alkyl and hydroxyalkyl groups containing 1 to 3 carbon atoms.

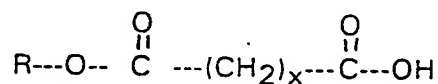
Useful amphoteric surfactants include derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds in which the aliphatic moieties can be linear or branched, or two of which can join to form a cyclic compound, provided that at least one of the constituents comprises or

- 5 contains a hydrophobic group containing from about 8 to 22 carbon atoms and the compound also contains an anionic water solubilising group, often selected from carboxylic, sulphate and sulphonates.

- Non-surfactant thickeners which may be employed comprise cross linked poly(acrylates), natural gums such as xanthan or rhamsan gum,  
10 cellulose derivatives such as carboxymethyl cellulose and silicates.

The process for preparing storage stable, aqueous acidic solutions according to the present invention comprising at least one ester peracid, comprises contacting an aqueous solution of one or more carboxylic compounds having the general formula:

15



- where x is from 1 to 4, R represents an alkyl group having from 1 to 4  
20 carbons, and x is from 1 to 4, with an inorganic peroxygen compound at a pH of less than 4 until at least some ester peracid is formed. The contact is normally effected at a temperature of from about 0°C to about 50°C, and in many embodiments is effected at a pH of 3 or less, particularly preferably 2.5 or less. Where the pH of the resultant ester peracid solution produced is less  
25 than 1, its pH is adjusted to be in the range of from 1 to 5.

- The inorganic peroxide, which is preferably hydrogen peroxide but may be a persalt such as sodium perborate mono and tetrahydrates, can be present in an equimolar ratio to the ester acid or acid derivative, but in many cases it is desirable to employ a molar excess of the inorganic peroxide. It will be  
30 appreciated that as the solution of ester peracid produced will tend to form an equilibrium composition, the choice of concentrations of the starting materials will to a large extent determine the final composition produced, unless subsequent processing, e.g. dilution, cause this to be changed.

- In certain embodiments where particularly rapid formation of the ester  
35 peracid is desired, the process for preparing storage stable, aqueous acidic solutions according to the present invention can be carried out in the presence of a catalytic amount of a strong acid, for example sulphuric acid, phosphoric acid and organic sulphonic acids such as methane sulphonic acid, to increase

the rate of formation of the ester peracid by lowering the solution pH. A pH in the range of from 0 to 1 is often employed. When employed, the strong acids will often be present in an amount ranging from 0.1 to 5% by weight of the solution. However, it will be recognised that the presence of a strong acid species causes relatively rapid hydrolysis of the ester function. Loss of the ester function not only directly causes loss of ester peracid, but also indirectly, by removing ester acid from the equilibrium, which causes ester peracid to revert to ester acid and hydrogen peroxide. Therefore, where a strong acid is employed, to produce a storage stable solution of an ester peracid, the strong acid should be neutralised by the addition of a corresponding amount of alkali. Alkalis that can be employed for this neutralisation include in particular alkali metal hydroxides and ammonia, particularly sodium hydroxide. In preferred embodiments of the present invention, a strong acid catalyst is employed, and the solution allowed to react in the presence of the strong acid until the ester peracid concentration reaches the desired concentration. At this point, alkali is then added to raise the pH of the solution to a value where the catalytic production of ester peracid is reduced or prevented, and the hydrolysis of the ester is also reduced or prevented, often a pH in the range of from 1.5 to 5, and particularly from 2.5 to 4, for example a pH of from 3 to 3.5.

In another preferred embodiment, the ester peracids according to the invention are prepared by controlled addition of an aqueous solution of hydrogen peroxide, having a concentration of up to 90% w/w and often greater than about 30% w/w, preferably from about 65% to about 88% w/w hydrogen peroxide to an aqueous solution of the ester acid starting material plus any other optional components with gentle agitation. Preferably, ambient temperature is employed, with typical values ranging from about 10°C to about 30°C. The time required to allow the ester peracid solution to reach equilibrium will depend on many factors, including the temperature and the presence and amount of any acid catalysts employed. Typical times are often between 1 day and about 30 days.

In a particularly preferred embodiment, the source of ester acid starting material comprises a mixture of the monomethyl esters of succinic, adipic and glutaric acid.

In some embodiments of the present invention, the ester acid is obtained in situ by hydrolysis of a diester, optionally in the presence of the inorganic peroxygen compound. Conditions similar to those employed for the strong acid catalysed production ester peracid are employed, followed by subsequent addition of alkali to mitigate against the detrimental effects of the

strong acid on the ester function. The advantage of such an approach is that it enables the more readily available diesters to be employed as starting materials.

The method for disinfection according to the present invention  
5 comprises contacting the substrate to be disinfected with a solution a storage stable, aqueous acidic solution of an ester peracid, or prepared from one. The solution may be employed without dilution, or may be diluted. When the compositions are diluted, the dilution is usually chosen to give a concentration of ester peracid in solution of between about 1 part per million and 10,000  
10 parts per million, depending on the substrate.

The disinfecting method may utilise a very wide range of temperatures, typically ranging from about 4°C to the boiling point of the solution employed as a disinfectant. In many cases, especially if the disinfectant is being applied manually using, e.g. a cloth, the temperature will be limited by the maximum  
15 temperature which can be tolerated comfortably by the operative, and is unlikely to be greater than 60°C.

The disinfection process can be employed to treat a wide range of substrates. Many of the treatable substrates are either liquid or solid. A contaminated gaseous substrate can be treated conveniently by spraying with  
20 a dilute solution of the invention biocidal combination or by bubbling the gas through a bath of the invention peracid solution. One type of liquid substrate comprises micro-organism contaminated aqueous media such as recirculating process waters, or aqueous effluents prior to discharge. Such process waters and effluents occur in many different industries and can be contaminated by  
25 bacteria, algae, yeasts and more rarely by viruses. Without limiting to the following industries, contaminated process waters are prevalent during the processing of plant and animal materials, including the paper and pulp industries, food processing eg the sugar refining industry, brewing, wine-making and alcohol distilling industries, effluents from straw treatments,  
30 discharges from sewage treatment works, including partially treated or merely filtered discharges of sewage through pipelines extending out to sea, meat processing factories, carcass rendering activities and from the rearing of livestock. Other liquid substrates include irrigation water in the horticulture industry. A further important source of contaminated aqueous media  
35 comprises cooling waters either industrially or arising from air conditioning units installed in large buildings; such as hotels, offices and hospitals. The invention compositions can be employed to treat non-aqueous liquid media, such as cutting oils.

Notwithstanding the foregoing, the invention compositions are seen as of particular value for disinfection in those areas which come into contact with humankind. Thus they can be employed to disinfect solids, including hard surfaces, or contaminated articles intended for re-use in the food processing, animal rearing, horticulture, catering, domestic or hospital environments. Hard surfaces can be made from metals, wood, ceramics, glass, and plastics and can include work-benches, walls, floors, sanitary ware, plant or apparatus, containers, tools, machinery, plant and pipework. It will be recognised that for such hard surfaces, it is often convenient to immerse smaller articles in a solution of the invention biocidal composition, and for larger applications, a spray or the like distribution means can be easier to employ. The process can also be contemplated for disinfecting water absorbent materials such as infected linen or especially soiled babies' nappies that are often made from terry towelling. The invention compositions can be used to disinfect harvested plants or plant products including seeds, corms, tubers, fruit, and vegetables. Alternatively, the invention compositions can be used to treat growing plants, and especially crop growing plants, including cereals, leaf vegetables and salad crops, root vegetables, legumes, berried fruits, citrus fruits and hard fruits.

It will none the less also be recognised that the peracid solutions produced by the invention process may also be employed, if desired, for the other purposes for which peracids are used, including bleaching or as a bleach additive in washing processes.

Having described the invention in general terms, specific embodiments thereof will now be illustrated by way of example only.

Example 1. Preparation of monomethyl perglutarate (MMPG)

Aqueous solutions comprising 10% w/w monomethylglutarate (MMG) and 10% w/w  $H_2O_2$  (Sample A), 10% w/w MMG and 20% w/w  $H_2O_2$  (Sample B), 20% w/w MMG and 10% w/w  $H_2O_2$  (Sample C), 20% w/w MMG and 20% w/w  $H_2O_2$  (Sample D), 30% w/w MMG and 10% w/w  $H_2O_2$  (Sample E), and 30% w/w MMG and 20% w/w  $H_2O_2$  (Sample E) were prepared by dissolving monomethylglutarate in water. To this solution was added with gentle stirring, the required amount of hydrogen peroxide (85% w/w) over a period of 10 minutes. The solutions each had a pH in the range of 1.5 to 2. The solutions were then stored at ambient temperature for 12 days and analysed by HPLC at intervals during this storage. The HPLC analysis employed an Apex octadecyl column (25cm, 5 microns) available from Jones Chromatography. The eluent was 75 : 25 water plus 0.25% acetic acid : methanol at an elution rate of 1

ml per minute. Ultra-violet detection at 210 nm was employed. The analysis showed a peak after 6.8 minutes which was attributed to monomethylperglutarate. To confirm this as a peracid peak, addition of thiodiglycol to the sample caused this peak to disappear. In addition to the 5 MMPG, the concentrations of monomethylglutarate (MMG), glutaric acid (GA) and perglutaric acid (PGA) were also monitored. The results are given in Table 1 below.

Table 1. Analysis of MMPG Samples (All % w/w)

Sample	Time (days)	% MMG	% GA	% PGA	% MMPG
10 A	5	8.8	0.9	0.13	0.17
	12	7.85	1.46	0.29	0.4
	21	7.6	2.0	0.15	0.24
15 B	5	8.1	0.8	0.31	0.73
	12	7.09	1.07	0.65	1.2
	21	6.86	1.59	0.63	0.93
20 C	5	17.3	1.98	0.2	0.47
	12	15.84	3.06	0.44	0.66
	21	15.1	4.37	0.22	0.39
20 D	1	18.5	1.1	trace	0.36
	5	15.8	1.58	0.78	1.8
	12	13.48	1.98	1.52	3.02
	21	12.56	2.77	1.73	2.92
25 E	1	27.4	1.65	trace	trace
	5	26.1	2.58	0.36	1.0
	12	24.2	3.99	0.6	1.23
	21	22.8	6.3	0.32	0.64
30 F	1	27.6	1.56	0.2	0.59
	5	23.6	1.13	1.1	3.1
	12	20.3	2.85	2.1	4.77
	21	19.59	4.22	2.12	4.05

Analysis of the solutions by titration with ceric sulphate solution showed that 35 after 21 days, Sample A comprised 9.7% w/w H<sub>2</sub>O<sub>2</sub>, Sample B comprised 19.5% w/w H<sub>2</sub>O<sub>2</sub>, Sample C comprised 8.8% w/w H<sub>2</sub>O<sub>2</sub>, Sample D comprised 19% w/w H<sub>2</sub>O<sub>2</sub>, Sample E comprised 8.5% w/w H<sub>2</sub>O<sub>2</sub>, and Sample F comprised 17.2% w/w H<sub>2</sub>O<sub>2</sub>. The results clearly show the storage stability of

the solutions according to the present invention. The storage stability results for samples B, D and F, ie those samples comprising about 20% w/w hydrogen peroxide, are particularly advantageous.

5 Comparison 2. Preparation of monomethyl perglutarate (MMPG) in the presence of strong acid, without subsequent pH adjustment

- 5.39g of monomethyl glutarate, 0.59g sulphuric acid (98% w/w) and 0.189g hydroxyethylidenediphosphonic acid, commercially available in the UK under the Trade name DEQUEST 2010, were dissolved in 37.59g of demineralised  
10 water. To this solution was added with gentle stirring, 5.99g of hydrogen peroxide (85% w/w) over a period of 10 minutes, producing a solution with a pH of about 0.5. The solution was then stored for 2 weeks at room temperature (ca 20°C). Analysis of the solution by the HPLC method given in Example 1 above showed that after 1 day, a mixture comprising MMPG and  
15 PGA an approximately 1 : 1 w/w ratio had been produced. However, after 2 weeks, substantially no MMPG remained. It was also observed that the concentration of MMG in the solution had significantly decreased, with a corresponding increase in glutaric acid concentration. These results indicated that the solution was not storage stable, probably on account of hydrolysis of  
20 the ester function in both MMPG and MMG.

Example 3. Preparation of MMPG plus Stabiliser

- 5.39g of monomethyl glutarate and 0.189g hydroxyethylidenediphosphonic  
acid, commercially available in the UK under the Trade name DEQUEST 2010,  
25 as stabiliser, were dissolved in 37.59g of demineralised water. To this solution was added with gentle stirring, 5.99g of hydrogen peroxide (85% w/w) over a period of 10 minutes. The solution was then stored for about 2 weeks. The solution was found to have no discernible odour.

30 Example 4. Preparation of monomethyl persuccinate (MMPS)

- Monomethyl succinate (5g) was dissolved in demineralised water (38.7g). To this solution was added 86% hydrogen peroxide solution (6g) over a 10 minute period with gentle stirring at room temperature and then hydroxyethylidenediphosphonic acid, commercially available in the UK under  
35 the Trade name DEQUEST 2010 (0.18g). The solution was allowed to stand for about 2 weeks, and was found to have no discernible odour.

Example 5. Preparation of monomethyl ester peracid from mixture of monomethyl esters of adipic, glutaric and succinic acids

Monomethyl glutarate (3.3g), monomethyl adipate (0.6g) and 1.2g monomethyl succinate were dissolved in demineralised water (38.7g). To this solution was added 86% hydrogen peroxide solution (6g) over a 10 minute period with gentle stirring at room temperature and then hydroxyethylidenediphosphonic acid, commercially available in the UK under the Trade name DEQUEST 2010 (0.18g). The solution was allowed to stand for about 2 weeks and was found to have no discernible odour.

10

Example 6. Disinfection Trials

The solutions prepared in Examples 3, 4 and 5 were screened for activity against bacteria (Pseudomonas aeruginosa and Staphylococcus aureus) and a yeast (Saccharomyces cerevisiae) employing the method described by M. G. C. Baldry in the Journal of Applied Bacteriology, 1983, vol 54, pp417 to 423, with a contact time of 5 minutes at 20°C. The pH of the solutions was varied as detailed in Table 3 below. The solutions were employed at 20 ppm peracid avox against the bacteria and at 50 ppm peracid avox against the yeast. Comparative tests were also carried out employing the same concentrations of peracetic acid by weight prepared by dilution of a peracid solution containing 1% w/w peracetic acid, 6% w/w hydrogen peroxide and 9% w/w acetic acid. The results of the trial are given in Table 2 below. Table 2 also includes comparative results under the same conditions against the yeast Saccharomyces cerevisiae for monoperglutaric acid solution (PGA), monopersuccinic acid solution (PSA) and a solution comprising a 45 : 27 : 27 weight ratio of monoperadipic acid : monoperglutaric acid : monopersuccinic acid (AGS).



Table 2. Results of Disinfection Trial

		Logarithmic Reduction Factor								
			Ps. aeruginosa			Staph. aureus		Saccha. cerevisiae		
5	Example	pH	5	6	9	5	6	5	6	9
	3		5.0	5.0	5.3	5.4	5.4	5.0	4.3	3.1
	4		5.3	5.0	5.1	5.4	5.5	5.1	5.2	3.6
	5		5.0	5.1	5.0	5.5	5.2	(not measured)		
10	PAA		5.0	4.9	5.0	5.4	5.0	5.5	5.3	3.0
	PGA							<3.0 nm		<3.0
	PSA							<3.0 nm		<3.0
	AGS							<3.0 nm		<3.0

15

nm = not measured

The results showed that against the bacteria and the yeasts, the ester peracid solutions according to the present invention gave a disinfection performance that was broadly comparable to that of peracetic acid. The good performance achieved against the yeasts is particularly surprising, given the poor activity of the PGA, PSA and AGS solutions. During the disinfection trial, it was observed that the odour of the peracetic acid solution was unpleasant, but that the odour from any of the solutions according to the present invention was not discernible, thus demonstrating that, on an equivalent performance basis, the compositions according to the present invention demonstrate lower odour.

#### Example 7. Preparation of monobutyl perglutarate

Monobutyl perglutarate was prepared by the method of Example 3 except that monobutyl glutarate (prepared by reaction between butan-1-ol and glutaric acid at a 1 : 1 mole ratio) was employed. After standing for 1 day, the solution was analysed and found to comprise 0.08% monobutyl perglutarate and 10.2% hydrogen peroxide. After 2 weeks storage at room temperature, the solution composition was found to be the same, within the limits of experimental error. The composition had no discernible odour.

Example 8. Preparation of monobutyl persuccinate

Monobutyl persuccinate was prepared by the method of Example 3 except that monobutyl succinate (5g) (prepared by reaction between butan-1-ol and succinic anhydride at a 1 : 1 mole ratio) was employed. After standing for 1 day, the solution was analysed and found to comprise 0.05% monobutyl persuccinate and 10.9% hydrogen peroxide. After 2 weeks storage at room temperature, the solution composition was found to comprise 0.12% monobutyl persuccinate and 10.4% hydrogen peroxide. The composition had no discernible odour.

10

Comparison 9. Preparation of mono-octyl persuccinate

Mono-octyl persuccinate was prepared by the method of Example 5 except that mono-octyl succinate (prepared by reaction between octan-1-ol and succinic anhydride at a 1 : 1 mole ratio) was employed.

15

Examination of the solution produced showed that it had formed a 2 phase system.

Example 10. Disinfection Trials

The solutions prepared in Examples 7 and 8 were screened for disinfection activity by the same general method as in Example 6 above. The pH of the solutions was varied as detailed in Table 3 below. The results of the trial are given in Table 3 below.

25 Table 3. Results of Disinfection Trial

30	Solution	pH	Logarithmic Reduction Factor								
			Staph. aureus			Ps. aeruginosa		Saccha. cerevisiae			
			5	6	9	5	6	5	6	9	
	7		4.0	3.8	3.9	4.2	4.1	> 5	< 2.5	3.4	
	8		4.0	3.9	3.9	4.4	3.9	> 5	> 5	> 5	
	PAA		4.1	3.9	3.8	4.3	4.3	> 5	> 5	< 2.5	

The results showed that against the bacteria, the ester peracid solutions according to the present invention gave a disinfection performance that was broadly comparable to that of peracetic acid. Against the yeasts, the disinfection performance was again at least comparable with peracetic acid,

and in the case of the solution of Example 8 at pH 9, was markedly superior to peracetic acid. This represents surprisingly good performance as >C4 aliphatic peracids are known to have very poor activity against yeasts. During the disinfection trial, it was again observed that the odour of the peracetic acid solution was unpleasant, but that the odour from any of the solutions according to the present invention was not discernible, thus demonstrating that, on an equivalent performance basis, the solutions according to the present invention demonstrate lower odour.

10 Comparison 11.

A solution of the same composition as Example 1, sample A was prepared, except that the solution was buffered to pH 4 on addition of the hydrogen peroxide. The solution was observed to contain substantially no ester peracid after 14 days storage at room temperature.

15

Comparison 12.

A solution of the same composition as Example 1, sample A was prepared, except that the pH of the solution was adjusted to 0.5 on addition of the hydrogen peroxide. The solution was observed to contain substantially no

20 ester peracid after 14 days storage at room temperature.

The results of Comparisons 11 and 12 demonstrate the importance of control of the pH during the preparation of the compositions according to the present invention.

25

Example 13 and Comparison 14

A parent solution of the same composition as Example 1, sample A was prepared, except that the solution also comprised 1% sulphuric acid. The pH of the solution was about 0.5. After 1 day's storage at room temperature, the solution was analysed by the HPLC method of Example 1. The solution was divided into 2 portions. In Example 13, the pH of the solution was increased to be about 2 by the addition of 47% w/w sodium hydroxide solution. In Comparison 14, the pH of the solution was not adjusted. The 2 portions were stored at room temperature for a further 8 days (ie 9 days storage in total).

35 The portions were then analysed by the HPLC method of Example 1. The results are given in Table 4 below.

Table 4

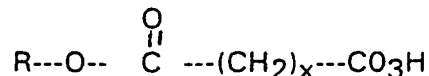
Sample.	Time (days)	% MMG	% GA	% PGA	% MMPG
Parent	1	5.69	2.97	0.94	0.4
Example 13	9	5.67	3.65	0.29	0.39
5 Comp 14	9	1.9	5.5	2.36	0.21

The results show clearly that after 9 days storage, the solution of Example 13 retains substantially the same MMPG concentration as the Parent solution, whereas that of Comparison 14 had reduced to almost half. This

10 demonstrates the advantage of increasing the pH of solutions prepared by the use of a strong acid catalyst. It also demonstrates the superior stability of the aqueous acidic solutions according to the present invention.

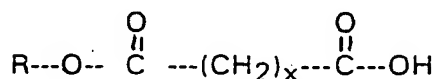
## Claims.

1. Storage stable, aqueous acidic solutions having a pH in the range of from 1 to 5 comprising at least one ester peracid having the general formula:



where R represents an alkyl group having from 1 to 4 carbons and x is from 1 to 4.

2. A solution according to claim 1, characterised in that the pH of the solution is from 1.5 to 4.
3. A process for preparing storage stable, aqueous acidic solutions comprising at least one ester peracid, characterised in that the process comprises contacting an aqueous solution of one or more carboxylic compounds having the general formula:



where x is from 1 to 4 and R represents an alkyl group having from 1 to 4 carbons with an inorganic peroxygen compound at a pH of less than 4, preferably 3 or less, until at least some ester peracid has been produced, and, thereafter, where the pH of the resultant ester peracid solution produced is less than 1, its pH is adjusted to be in the range of from 1 to 5.

4. A process according to claim 3, characterised in that the inorganic peroxygen compound comprises hydrogen peroxide.
5. A process according to claim 4, characterised in that the hydrogen peroxide has a concentration of from about 65% to about 88% by weight.
6. A process according any one of claims 3 to 5, characterised in that contact occurs at a pH of 2.5 or less.
7. A process according to any one of claims 3 to 6, characterised in that a strong acid catalyst is employed at a pH of from 0 to 1, and after the ester

peracid has reached the desired concentration, the pH is adjusted to 1.5 to 5 by the addition of alkali.

8. A solution or process according to any preceding claim, characterised in that x is 2, 3 or 4.
9. A solution or process according to any preceding claim, characterised in that R is a methyl group.
10. A solution or process according to any preceding claim, characterised in that the ester peracid comprises from about 0.0001 to about 15% by weight of the composition.
11. A solution or process according to claim 10, characterised in that the ester peracid comprises from about 0.1 to about 5% by weight of the solution.
12. A solution or process according to any preceding claim, characterised in that the ester peracid is monomethylperglutaric acid.
13. A solution or process according to any one of claims 1 to 11, characterised in that the ester peracid is monomethylperadipic acid.
14. A solution or process according to any one of claims 1 to 11, characterised in that the ester peracid is monomethylpersuccinic acid.
15. A solution according to any one of claims 1, 2 or 8 to 14, characterised in that the solution comprises from 15 to 25% by weight hydrogen peroxide.
16. A method for disinfecting, characterised in that the method comprises contacting a substrate to be disinfected with an ester peracid solution, or obtained from an ester peracid solution, according to any one of claims 1, 2 or 8 to 15.
17. A method for disinfecting according to claim 16, characterised in that the concentration of ester peracid is from about 1 ppm to about 10,000 ppm of the composition.

# INTERNATIONAL SEARCH REPORT

Inter- national Application No  
PCT/GB 95/01398

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07C409/24 C07C407/00 A01N37/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 324.626 (AGENCE NATIONALE DE VALORISATION DE LA RECHERCHE) 15 April 1977 cited in the application see the whole document -----	3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

31 August 1995

Date of mailing of the international search report

- 6. 09. 95

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/GB 95/01398

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2324626	15-04-77	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)